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ANNUAL AFOSR CHEMISTRY PROGRAM REVIEW(21ST), FY75-76, (U)
JUL 77 R W HAFFNER, D W ELLIOTT

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21st AFOSR Chemistry

Program Review

FY 75 - 76

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 76-0001	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 21st ANNUAL AFOSR CHEMISTRY PROGRAM REVIEW, FY75 AND 76		5. TYPE OF REPORT & PERIOD COVERED Scientific Special
7. AUTHOR(s) RICHARD W. HAFNER, Editor		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Directorate of Chemical Sciences Air Force Office of Scientific Research Air Force Systems Command, USAF Bolling AFB, Washington, D.C., 20332		8. CONTRACT OR GRANT NUMBER(s) In-house
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2303 61102F
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 1 July 1977
		13. NUMBER OF PAGES 233
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <div style="display: flex; justify-content: space-between;"> <div> Basic Research Program Chemistry U.S. Air Force Air Force Office of Scientific Research Directorate of Chemical Sciences </div> <div> Chemical Instrumentation & Techniques Surface Chemistry Chemical Approaches to New Thermally Stable Materials Research in Gas Phase Kinetics </div> </div>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This review provides a record of research in progress, along with illustrative achievements resulting from the basic research program of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFSC). The first section of the three principle sections presents various technical aspects. It contains articles on Air Force research in Molecular Dynamics, Structural Chemistry and Chemical Instrumentation plus a report on Electrochemistry submitted by the European Office of Aerospace Research and Development. The second section contains program statistics. The third section consists of research efforts completed in Fiscal Year 1975 and 1976.		

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AFOSR

Chemistry Program Review (21st)

FY75-76,

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July 1977

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238p.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)

DIRECTORATE OF CHEMICAL SCIENCES

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Acknowledgments

This review is due to the combined efforts of the technical and secretarial staff of the Directorate of Chemical Sciences. Multiple thanks go to Mrs. Iris Worley and Miss Gloria Chodos for their efforts in typing the drafts. The Editor wishes to express special appreciation to Mrs. Marlys Dillon for the many hours devoted to typing the final copy, preparing the article headings, and the preparation of the book into its final form for printing.

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Mission

The Directorate of Chemical Sciences of the Air Force Office of Scientific Research has the mission to encourage and support fundamental research designed to increase understanding of the science of chemistry, to stimulate the recognition of new chemical concepts, and to provide for early exploitation of their military implications.

The Directorate obtains and maintains for the Air Force a diversified program of chemical research through support of scientists in promising original endeavors of their own choosing. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways the Directorate aids the Air Force in its maintenance of technological superiority.

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DEPARTMENT OF THE AIR FORCE
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TO: Members of the Chemistry Research Evaluation Panel

Gentlemen:

This time we are presenting you with a big package. We are including in this review the completed project summaries for FY75, FY76 periods, and an additional three month interval, known as 7T period, which accounts for the change in the fiscal year.

Since our last Review, we have had some changes. Besides the fiscal year change of the government to 1 October, our office has moved to Bolling Air Force Base, and we also have those inevitable changes in our personnel. Mrs. Marlys Dillon is the new secretary to the Director, and Dr. Donald Ulrich and Lt Colonel John Viola are the new program managers of the Structural Chemistry and Chemical Dynamics programs, respectively.

In addition to the above, the responsibilities of AFOSR have been increased. The AFOSR Director is now responsible for the accountability of all the basic research funds (6.1) in the Air Force. He in turn has allocated to the directors of the various scientific disciplines the respective responsibilities. This, in turn, imposes additional work loads on the program managers in terms of travel, paperwork, and selectivity of high quality and relevant proposals.

It is this latter part that we have leaned on you panel members for assistance. We are indeed grateful to you for helping us select the best ideas and the best man, whose research results are awaited with interest by the Air Force and by the scientific community. Thank you.

Gratefully,

Donald L. Ball

DONALD L. BALL
Director, Chemical Sciences

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A Status Report From Abroad

ELECTROCHEMISTRY AT THE NORWEGIAN INSTITUTE OF TECHNOLOGY

(This article was written by Major D. E. Dodds, former Chief of Physical and Environmental Sciences, European Office of Aerospace Research, London, England.)

Norway's only technical university, Norges Tekniske Høgskole (NTH), was established at Trondheim in 1910. The objectives of the NTH are to provide education for engineers and architects and to further the development of those branches of science and art which are pertinent to technological education and activity. NTH consists of eight Departments: Architecture, Earth Sciences and Metallurgy, Civil Engineering, Electrical Engineering, Chemistry, Mechanical Engineering, General Sciences, and Naval Architecture. Each Department in turn is divided into several institutes. The Department of Chemistry has ten institutes: Inorganic, Organic, Industrial, Physical, Chemical Engineering, Cellulose Technology, Industrial Electrochemistry, Applied Biochemistry, Silicate Science, and Marine Biochemistry.

There are a number of research institutes closely associated with NTH. The most important is SINTEF (Foundation for Science and Industrial Research). The aim of this independent, non-profit organization is to place the research facilities of NTH at the service of industry and to coordinate NTH-industry relations.

The Institute of Inorganic Chemistry, directed by Professor Harald A. Øye, has fourteen active research projects, mostly allied to the industries for production of aluminum and magnesium. About 50% of the support for the Institute comes from the government for teaching and the remainder from grants by science councils, industry, NATO, etc., for research projects. These grants are administered through SINTEF.

Research projects include complex formation in molten and solid halides, theory of aluminum electrolysis, convection and current efficiency studies in commercial aluminum reduction cells, characterization of oxychlorination catalysts for producing vinyl chloride, petrochemical reactions in molten salt catalysts, formation of aluminum carbide, phase relations in fluoride systems, and matrix spectroscopy studies of the configuration of alkali/aluminum and alkali/iron fluorides. This Institute has developed an oscillation type viscometer capable of determining the absolute viscosity of low viscosity melts at elevated temperatures. This instrument is also able to measure viscosities of liquids having high vapor pressures such as the chloroaluminates. NTH is involved in a National Bureau of Standards program to recommend absolute viscosity values of some test molten salts.

NTH has initiated work on molten salt catalyzed conversion of simple hydrocarbons. Current studies involve oxychlorination of ethylene and the effect of catalyst carriers on conversion. Future work will concentrate on molten salt catalysis in bulk. Molten salt catalysts can give good product selectivity combined with high catalytic activity and may lead to unique synthetic processes.

The Institute of Industrial Electrochemistry, headed by Professor H. Holtan, is primarily engaged in research on molten salt electrolysis and corrosion. As in the Institute of Inorganic Chemistry, research is directed at understanding electrochemical processes and improving efficiencies of aluminum and magnesium production methods. Projects include: determining the activities of AlCl_3 in NaAlCl_4 melts, electrode reactions in NaCl/AlCl_3 , and kinetics of halogen

2

evolution reactions. Techniques employed in electrode studies include current density/potential, double layer capacitance, cyclic voltimetry and anodic stripping. Work on $\text{NaCl}/\text{AlCl}_3$ indicates that the primary discharge reaction is the rate controlling process in AlCl_3 rich compositions, but the mechanism changes in NaCl rich compositions. Also the nature of complexes in the double layer changes with temperature. Other projects to be initiated include the study of aluminum deposition reactions and the investigation of additives for reducing the melting point of salt mixture. This Institute is also investigating the corrosive effects of molten salts on such metals as aluminum and steel.

Several projects in the Institutes of Inorganic and Electrochemistry directly complement the Air Force's research on molten salt thermal batteries. For example, the F. J. Seiler Laboratory is studying the vapor pressure and electric conductivity of chloroaluminate melts around 200°C with particular interest in AlCl_3 rich systems. Øye's group is doing similar research on AlCl_3 poor systems at 800°C . Together, these programs provide a more complete understanding of the properties of chloroaluminates. In addition, the Seiler Laboratory is well equipped to measure densities of molten salts, but cannot measure viscosities of volatile melts. Conversely, NTH has a unique capability for the latter but none for the former.

NTH has outstanding facilities and exceptional expertise in molten salt electrochemistry and processes. Electrochemistry research at NTH, as most research in Norway appears to be, is directly influenced by Norwegian industries, particularly aluminum and magnesium production and the future availability and exploitation of North Sea oil. Nevertheless, basic investigations are directly applicable to Air Force research objectives for thermal batteries. Closer Air Force/NTH cooperation has been initiated and will undoubtedly increase.

Chemical Instrumentation

D. W. Elliott

Modern science has developed to the stage that it exists today because of the development of new tools which has assisted this existence in the exploration of the underlying fundamental scientific principles. Included in this development picture is the continuing improvement in the performance of analytical instruments which is steadily lowering the limits of detectability. Many instrumental methods are capable of microgram and nanogram limits, while selected methods have demonstrated picogram (10^{-12} g) and femtogram (10^{-15} g) limits. But it should be emphasized that detection limits, alone, indicate little about the complexity of the analysis or the difficulty of detecting specific compounds in a conglomerate of interferents. The sensitivity of a method to specific compounds can vary widely. This is probably the most important factor in selecting an analytical method. In this Chemical Instrumentation Program one of our objectives is to nurture and promote new chemical methods, techniques, and instrumentation, that will give the scientific community a handle on gathering scientific information which has been ascertained to be relevant to the solution of Air Force problems. It is with the foregoing in mind that new research ideas in this area are given priority consideration in the selection process for inclusion in the program.

A sampling of a few accomplishments in the program follow:

Professor J. D. Winefordner at the University of Florida has utilized tunable dye lasers (TDL) as an excitation source in molecular luminescence spectrometry (MLS). Although the use of TDL had often been suggested, it was Winefordner's group that put it to practice. They and others had used it previously in atomic fluorescence spectrometry.

The criteria for an ideal source for MLS should be:

(1) sufficiently intense as to result in near saturation of the excited electronic state, in order to minimize source fluctuation errors and environmental changes, i.e., variations in the quantum efficiency, and to maximize the linear range of the analytical calibration curve; (2) of sufficiently narrow tunable spectral output to enable excitation resolution of molecules; (3) and sufficiently safe and easy to operate and maintain, and economical to purchase and maintain, so that workers in the field will utilize the source for research and routine measurements. The pulsed, tunable dye laser seems to fulfill or nearly fulfill requirements.

The University of Florida experimental set-up consists of a pulsed TDL, a conventional molecular fluorescence cell assembly maintained at room temperature, a 0.3 m Czerny-Turner monochromator, an EMI 9681B photomultiplier and a boxcar integrator-recorder readout. A 110 mm focal length, biconvex, fused silica lens was used to focus the laser beam at the center of the 1 x 1 cm quartz cell. A 1:1 image of the cell was formed at the entrance slit of the emission monochromator with a similar quality lens. After tuning the laser for maximum fluorescence signal with the molecule of interest, the cross-sectional area was observed visually on a

calibrated grid with a microscope. The total flux of the laser was measured with a calibrated vacuum photodiode (ITT 4000 S-5) and calibrated neutral density filters (Ealing Corp., Cambridge, Mass.). The laser duration was measured with a sampling oscilloscope (Tektronix 545A with 1S1 plug-in) connected to the boxcar integrator. The spectral bandwidth of the laser beam was measured by scattering the laser beam into the monochromator with a Teflon sheet and scanning the monochromator with 0.01 nm minimal bandpass.

The effect of laser irradiance upon the absorption and fluorescence signals was observed by two means: (i) the signals were measured with and without the focussing lens between the laser and sample cell; and (ii) the signals were measured with and without neutral density filters between the laser and the sample cell.

From theoretical and experimental considerations, it seems evident that the pulsed tunable dye laser is capable of approaching saturation conditions for many organic molecules: Experimental results shown in Table 1, in which the absorption signal for fluorescence depends upon the source irradiance and the fluorescence signals do not vary linearly with the source irradiance incident upon the sample, are qualitatively consistent with those predicted for a saturated system. At high source irradiances incident upon the sample, the absorbance is smallest and approaches a constant value as the source irradiance decreases. In agreement with these results, the ratio of fluorescence signal obtained without neutral density filter between the sample and the source to that with a neutral density filter increases nonlinearly as the neutral density filter becomes more opaque. Similar results were obtained for acridine and quinine sulfate.

Table 1. Effect of laser irradiance upon the absorption and fluorescence signals of fluorescein, quinine sulfate and acridine.

Molecule	Variable filter/Lens	Wavelengths (nm)		Absorbance*	Fluorescence ratio,* F_o/F_x
		Excitation	Emission		
Fluorescein	No filter/Lens	480.0	514.3	0.22	1.0
Fluorescein	50% filter/Lens	480.0	514.3	0.23	1.5 (1.3+)
Fluorescein	10% filter/Lens	480.0	514.3	0.38	6.6
Fluorescein	No filter/No lens	480.0	514.3	0.63	1.0
Fluorescein	10% filter/No lens	480.0	514.3	0.63	2.0
Acridine	No filter/Lens	359.5	415.2		1.0
Acridine	50% filter/Lens	359.5	415.2		1.87
Acridine	10% filter/Lens	359.5	415.2		8.6
Quinine	No filter/Lens	365.0	453.8		1.0
Quinine	50% filter/Lens	365.0	453.8		1.24 (1.35+)
Quinine	10% filter/Lens	365.0	453.8		3.82

* 10 ppm of respective solution, unless otherwise indicated.

† 10 ppb of respective solution.

Because of the simplicity of the experimental system, i.e., no excitation monochromator, because of the narrow spectral output, i.e., ~0.4 nm without frequency narrowing and much less with frequency

narrowing, and because of the good limits of detection with minimal efforts, it would seem that pulsed tunable dye lasers should have use in the analytical laboratory, particularly where excitation selectivity is needed. It should be possible to excite selectively one molecule in the presence of others. The N_2 -pulsed tunable dye laser also has the potential of additional selectivity through time-resolution resulting from its short (<10 nsec) pulse. Selectivity could also be increased through the use of excited state absorption and luminescence, as, with the dye laser, the first excited singlet state may be significantly populated.

For those molecules in which intersystem crossing takes place from higher vibronic levels of the excited singlet state, selective excitation to lower vibronic levels, e.g., of the 0-0 band, may increase the fluorescence signal level via improved quantum efficiency, or selective excitation to the higher vibronic levels may increase the phosphorescence signal.

Under saturation conditions, the tunable dye laser also has the potential of increasing the linear working range and also of decreasing the effect of the environment (e.g., quenchers) upon the analysis.

At Hughes Research Laboratories, Dr. Hong Sup Lim, and Dr. J. David Margerum have been studying dopant effects on dc dynamic scattering (DS) in a liquid crystal. The microscopic patterns of dc - DS show that the electrochemical properties of dopants determine the dominant charge injection reaction, direction of liquid crystal (LC) flow, and location of the LC turbulence. They have compared different dopants (an electron acceptor, an electron donor, and a non-reactive salt) in an ester LC. These results differ substantially from earlier microscopic observations, of dc-DS in other LC's, but are consistent with their studies showing that redox dopants (donors and acceptors which readily undergo reversible electrochemical reactions in the LC) give dc-DS at lower threshold voltages as well as giving higher scattering levels and much longer lifetimes than salt dopants.

A nematic LC designated as HRL-2N10 is used. It has a nematic range of about 18° to 55° , a dielectric anisotropy of $\epsilon_a = -0.12$ (25°C , 500 Hz) and a birefringency of $\Delta n = 0.14$ (25° , 545 nm). In the undoped state, it is highly resistive ($\rho = 3.8 \times 10^{11}$ ohm-cm at 100 Hz) and does not show DS effects. The salt dopant used is tetrabutylammonium trifluoromethanesulfonate (TBATMS); the acceptor is (2,4,7-trinitro-9-fluorenylidene)malononitrile (TFM); and the donor is di-n-butylferrocene (DBF).

Electrochemical studies in solvents containing 0.1 M tetrabutylammonium perchlorate show decomposition potentials (vs. saturated calomel electrode) of the LC components at about +1.7 V (in acetonitrile) for oxidation and -2.2 V (in dimethylformamide) for reduction. The formal reduction potentials (in acetonitrile vs. SCE) for the reversible electrode process of the redox dopants are quite low, e.g., 0.03 V for TFM and 0.32 V for DBF. Thus when the LC contains TFM or DBF, the electrochemical reactions of these dopants should be a dominant factor in the passage of current through the LC. This is confirmed by using a polarizing microscope to observe the direction of LC flow between electrodes. Test cells

(Fig. 1) are made by sandwiching the LC between a substrate containing two thin film transparent electrodes and a glass cover plate with a $51\text{ }\mu\text{m}$ thick Mylar spacer. This cell geometry is chosen to allow space for the back flow of the LC outside the area of observation, i.e., in the periphery of the cell where the field is low. The LC is aligned parallel to the surface of the glass and perpendicular to the electric field, by a rubbing technique. With TFM added, the LC flow is predominately from the negative to the positive electrode, while with DBF added the predominant LC flow is from positive to negative.. When equimolar mixtures are added, the LC flow in each direction is approximately balanced, which is also the case when the salt dopant is used. These flow patterns are observed by the movement of dust particles in the LC. The flow directions are also confirmed by studies in tubular cells with screen electrodes and side arm capillaries to indicate the pressure effect of the LC flow.

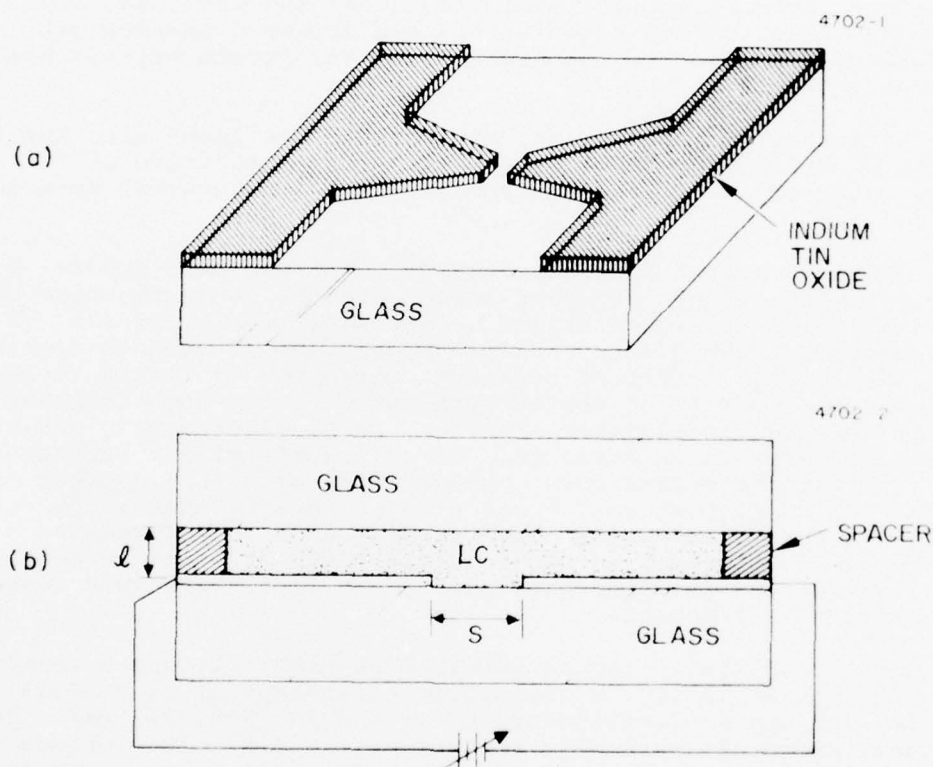


Figure 1. Test cells for microscopic pattern studies of dc-DS. (a) Substrate with electrodes. (b) Cross-section of assembled cell, with $S \sim 380\text{ }\mu\text{m}$ and $l = 51\text{ }\mu\text{m}$. The microscope view is from the top, perpendicular to the applied field.

The direction of the LC flow is consistent with a unipolar space charge injection followed by the propagation of the space charge under the influence of the applied electric field, as previously observed or discussed by others. The results indicate that in the presence of TFM unipolar injection of negative ions

is probably dominant ($\text{TFM} + \text{e}^- = \text{TFM}^-$), followed by the reverse reaction at the positive electrode. Similarly with DBF, unipolar injection of positive ions is probably dominant ($\text{DBF} = \text{DBF}^+ + \text{e}^-$) followed by the reverse reaction at the negative electrode. A simultaneous bipolar injection occurs when both redox dopants or when the salt is present. However, when the dopant is a non-reactive salt, LC radical ions are probably formed at the electrodes.

In the study of scattering patterns with the different dopants at various applied voltages, no scattering was observed with the salt dopant at 40 V.) With the salt dopant, the scattering pattern has a line structure which contains alternating lines originating from each electrode. Thin flow lines of LC are initiated from each electrode at the same time and propagate toward the opposite electrode. Dust particles move along the lines in the direction of the propagation, indicating that the lines are caused by LC flow. These effects are similar to Williams domains, in which the source of the LC hydrodynamic motion has been well analyzed. However, with a redox dopant the general appearance of the scattering pattern is quite different. Turbulent motions of LC are observed at lower voltages, without formation of a regular line structure. The turbulence is initiated from one electrode and propagates toward the other. Except at very high voltages, the turbulence does not reach the opposite electrode but remains localized near the electrode where it was initiated. The most interesting observation is that the turbulence is initiated from the negative electrode when the dopant is the donor and from the positive when the dopant is the acceptor, while the charge injection and the liquid crystal flow are in the opposite directions. Dust particles move from the rear of the non-turbulent electrode toward the turbulent electrode and travel across it.

When the redox dopant is a balanced mixture of the acceptor and donor, the turbulence occurs more randomly. At low voltages turbulence begins at both electrodes and also between them, although to a lesser extent. Regions of flow may appear, but the overall effect is more like a combination of pictures from the individual redox dopants than that of the salt dopant finger patterns. The onset of turbulence occurs at lower voltages with redox dopants (single or mixed) than with salt dopants, and the LC turbulence is greater at a given voltage. Similar results are observed with the same LC between transparent electrodes in conventional flat panel cells.

References:

Journal of Electrochemical Society (June 1976)

Structural Chemistry

DONALD R. ULRICH

The objective of the Structural Chemistry task is to establish the fundamental structure-property correlations in non-metallic materials as a basis for predicting the performance, properties and synthesis of new materials of high potential interest to the Air Force. The task encompasses programs in polymer, science, glass chemistry, solid state chemistry and carbon-carbon materials research.

The research in polymer chemistry is focussing on structural, containment and environment resistant materials with thrust areas in:

1. Structural adhesive and composite matrix durability.
2. Processing science of polymers.
3. Microstructure/property/processing relations of amorphous and semi-crystalline polymers.
4. Self-reinforced or ordered polymers.
5. Fuel tank sealant rheology and morphology.
6. Protective materials for spacecraft.

Dr. Roger Morgan of the McDonnell Douglas Research Laboratory has been investigating the basic relations between the chemical and physical structure, failure processes and mechanical response of polymeric glasses, in particular, epoxies. Epoxies have been shown to fail by a crazing process under tension. The modification of structure - property relations by fabrication procedures and environmental exposures are also being studied. These data will be utilized to understand the basic phenomena controlling the durability of epoxy adhesives and composites used as aircraft structural components. The crazing failure process in epoxies, in particular, the craze cavitation mechanism, has been shown to be significantly modified by absorbed water.

The principles underlying the processing mechanisms, structure and morphology of high temperature polymeric alloys are being studied by Dr. Ian Hay of the Celanese Research Company. Since the most stable Air Force polymer systems are relatively intractable and difficult to process by current fabrication techniques, the processibility by alloying with compatible polymers and monomers to yield combinations of polymers which are more readily fabricable and have high temperature properties similar to the major intractable components is being pursued.

In complementary research, Dr. Frank Karasz of the University of Massachusetts is determining how molecular structure and morphology on a supermolecular scale govern polymeric interactions and the resultant physical and mechanical properties. Research on the development of the specific principles for predicting compatibility and alloying in multi-component polymer systems is being conducted. In blends, for example, he has shown that processing can be crucially important with respect to properties of the end product.

Polymer films formed from a 50/50 blend of poly(2,6-dimethyl phenylene oxide) with a copolymer containing 43 more percent o-chlorostyrene and 57 more percent p-chlorostyrene can be homogeneous and transparent, when produced by annealing at 240°C, or phase-separated and cloudy if annealed at 270°C, and cooled rapidly. The mechanical properties of the two systems differ dramatically; the tensile strength of the homogeneous system was 5-10 times greater than that of the phase-separated film.

A remarkable feature of the latter is that this structure is developed in a few minutes (5-15) at 270°C, demonstrating that considerable mass transfer of high molecular weight constituents can occur over such time scales.

Dr. Karasz has shown that the tensile strength of blends presents a new criterion for compatibility of binary polymer systems in that compatible polymer pairs always display a maximum in tensile strength as a function of blend composition; incompatible systems display a minimum in this property. This effect is believed to be associated with mass densification.

Professor Donald R. Uhlman of the Massachusetts Institute of Technology is conducting research to provide insight into the important microstructural features of polymers, their dependence on processing variables, and their relations to mechanical and optical properties. Attention is being directed to (1) nodular structures in amorphous polymers, both thermoplastics and thermoset; (2) structure differences between bulk material and near-surface regimes in semicrystalline polymers; (3) crystallization behavior under high thermal gradients and its effect on structure; and (4) differentiation between adjacent re-entry folding and switch-board models for the basic structural units in semicrystalline polymers.

Understanding of the glass transition phenomena as related to structure is essential to the processibility of new polymer systems. Dr. Martin Goldstein of Yeshiva University has been studying the thermodynamics of the glass transition as related to the structure and the strength of secondary relaxation processes as related to annealing, the fictive temperature, and structural state of the amorphous phase.

The Air Force Materials Laboratory and AFOSR are jointly conducting research on ordered polymers for molecular or self-reinforced composites. Currently available aircraft structures fabricated from high strength fiber reinforced composites obtain their high strength from the fiber reinforcement of amorphous matrix resins wherein the fibers have been drawn to produce molecular alignment. However, aircraft structures fabricated from the unique high strength homopolymers will derive their high strength from the alignment or ordering of long chain polymer molecules in the polymer matrix.

Professor Guy Berry of Carnegie-Mellon University is studying the kinetics of polymerization of rodlike polymers. The research of Dr. Paul Flory at Stanford centers on the statistical thermodynamics of stiff chains directed toward models for semi-flexible chains, the theory of heterodisperserods, the application of theory to liquid crystals comprising anisometric species of low molecular weight, and the factors governing generation of phases of high molecular orientation in extended, stiff-chain polymers. Professor Fratini of the University of Dayton is conducting structural studies of ordered polymer systems and monomeric model compounds.

Operational and advanced Air Force systems employ hydraulic fluids, electrodynamic lubricants, fuels and propellants which are required to have superior physical, thermal and mechanical properties over broad temperature and pressure ranges. The basic principles and parameters governing the behavior of these fluid mixtures, their dependence upon temperature and pressure, and their correlation with molecular structure have not been understood. Dr. Jeri Jonas of the University of Illinois studied the high-pressure nuclear magnetic resonance relaxation of supercritical dense fluids. His research proved that transport and relaxation properties of simple fluids composed of molecules of spherical shape can be interpreted in terms of the hard sphere model of liquids. He also established the validity of the rough hard sphere model of liquids to describe transport processes and relaxation behavior in binary mixtures. As an extension of this work, Dr. Jonas is studying the dynamic structure of viscoelastic fluids and elastomers. This includes investi-

gating the dynamic processes at the molecular level of fuel tank sealants and correlating them with macroscopic properties to establish a guide for the development of better sealants. In conjunction with Dr. Jonas and AFML, Dr. Berry of Carnegie Mellon is studying how the rheological properties of sealants vary with the choice of polymer, type and amount of additives and environmental conditions.

The interaction of synchronous orbit satellites with its environment activates electrification and electrical discharge processes producing electromagnetic noise pulses and effluents which deteriorate satellite materials, surfaces and components. Dr. Joseph Nanevich of the Stanford Research Institute is performing research to understand the mechanisms underlying spacecraft charging in polymeric and other nonmetallic dielectrics. It is expected that his research will contribute to the establishment of guidelines for the design and modification of satellite materials which are not degraded by the effects of electrical charging and which will minimize disruptions in Air Force space systems mission performance. His approach is to: (a) study the nature, causes and effects of charging and discharging processes in typical spacecraft polymers and other nonmetallic dielectrics under orbital conditions; (b) determine the physics of critical electrostatic charging properties; and (c) study the methods for modification of materials properties to improve their in-space performance characteristics.

Glass chemistry research stresses the compositional and structural control of thermal expansion, mechanical strength and hardness, chemical durability, interactions with infrared and visible radiation, and the environmental sensitivity of properties.

For aircraft canopies, oxide glasses are laminated to organic polymers. Usually the expansion coefficients of organic polymers are much higher than those of oxide glasses. This mismatch in expansion can cause high stresses at the interface and can lead to delamination and cracking. High expansion glasses have been prepared at UCLA by Professor J. D. Mackenzie which show no cracking when cooled at 20°C. To increase the chemical durability (i.e., decrease the dissolution rate) the high expansion glasses containing sodium ions were ionexchanged in molten lithium nitrate. The thin layer of lithium-rich glass has much better chemical durability and hence acts as a protective layer. However, the expansion coefficient is controlled by the bulk of the glass which has high expansion. Thus new glasses with high expansion and good chemical durability have been developed.

The fundamental understanding of how structure influence optical properties of solids is vital for establishing the principles of laser hardened glass and if materials are used to reflect and/or scatter infrared radiation. Part of Dr. Mackenzie's studies involve the reflection of infrared by materials which are transparent in the visible part of the spectrum. His work in this area is presently concerned with the deposition of films of BeO on to glass surfaces and the study of the reflectivity of such films since crystalline beryllium oxide shows remarkable reflectivity in the 10 to 14 micron range of the infrared.

In complementary research, Dr. Larry Hench at the University of Florida has undertaken the systematic study of glass and glass-ceramics to determine the relationship of residual glass phase composition and distribution to the environmental sensitivity of the mechanical, dielectric and thermal properties. His research also includes sialon glasses and the establishment of non-destructive testing procedures for investigating residual glass content.

The objective of the solid state chemistry subtask is the systematic development of crystal chemistry methods for the prediction of chemical structures with electromagnetic properties in new organic, inorganic and molecular solids. Thrusts in molecular crystal chemistry, organic crystal chemistry, inorganic defect crystal chemistry and the study of the fundamental electro-optical properties of inorganic solids containing transition metal complexes constitute the systematic development of this area.

The objective of the research of Dr. Glenn A. Crosby of Washington State University is to utilize transition metal complexes and their charge-transfer excited states in inorganic solids to guide the design of new electronic materials with potentially useful electro-optical properties. The research encompasses chemical synthesis, luminescence spectroscopy, and the determination of the effects of external magnetic fields on excited solid state properties of complementary inorganic complexes whose electronic structures suggest the incidence of strong solid state interactions when the units are incorporated with solids. This includes an investigation of complexes that are highly colored but contain closed shell d¹⁰ ions. Spectroscopic investigation of new zinc compounds with the generic formula Zn(S-S)(N-N), Zn(S-L)₂(N-N) or Zn(N-N)X₂, where N-N indicates a bidentate heteroaromatic ligand, S-S an aromatic thiol, S-L an aromatic thiol, and X a halogen, confirms the existence of an interliquid transmetallic charge transition (ITCT) that is responsible for the deep and variable colors of these materials and for the diverse spectroscopic properties observed. Crosby's findings show that: (a) the ITCT excited state can be turned over a large frequency range; (b) the ITCT excited state has a small singlet-triplet split (300 cm⁻¹); (c) the ITCT excited state can modulate both the yield and the lifetime of both the fluorescence and the phosphorescence from the molecules; and (d) the distinct possibility exists of tuning the excited state to interact quadratically with an external magnetic field. This research shows great promise for designing new and unusual materials that will display huge charge separations in their excited states.

Dr. Elliott Bernstein of Colorado State University is pursuing research in molecular crystal chemistry to develop the characterization and understanding of cooperative solid state phenomena in molecular crystals. This includes experiments to: (a) identify and relate soft modes, lattice instabilities and structural magnetic and electrical phase transitions in molecular crystals; (b) to define the interaction of electromagnetic radiation and dipolar lattice and molecular modes in molecular solids, including ferroelectric and ferroelastic materials; and (c) to establish the existence or nonexistence of polaritons in molecular solid state chemistry and dynamic behavior.

The Office of Naval Research and AFOSR are jointly supporting a research program in carbon-carbon materials and structures. Carbon-carbon composites are the leading structural materials for rocket nozzles and missile nosetips and heat shields because of their high thermal stability, flexibility, light weight, chemical inertness, low thermal conductivity, dimensional stability, low electrical resistivity, nontoxicity, nonflammability and other attributes. The fabrication of carbon-carbon composites involves a series of operations starting with weaving carbon fiber bundles into an orthogonal fabric. This is followed by pressure impregnation of the preform with liquified coal tar pitch, carbonization and graphitization. The latter three steps are repeated as required to densify the composite or billet. The processing is common to composites for both rocket nozzle and reentry vehicle applications although each experiences different operational environments.

Reliability and materials availability have been identified as the pacing problem areas with carbon-carbon composite technology and performance. The ONR-AFOSR effort with a rocket nozzle technology focus entails fundamental research in composite process chemistry and modeling, mechanical behavior and reliability, constitutive properties, nozzle structural analysis and failure criteria, thermochemical properties and recession, alternate materials and non-destructive evaluation.

The goal of the Structural Chemistry task will be to establish the precursor and processing chemistry data base for carbon fibers and carbon-carbon composite materials.

Most grades of fibrous carbon are manufactured from the continuous filament rayon precursor. Because of the declining commercial market for this textile product in the United States, continued availability is no longer assured. Basic research in support of the evaluation and development of equivalent replacement materials will be initiated to preclude future shortages or production delays. The chemistry of the stabilization and graphitization of pitch, polyacrylonitrile and other precursors which can be converted into carbon fibers will be investigated. The chemistry of the systems as the fibers are processed through the various stages of conversion, mesophase development, how changes in the process conditions affect the microstructure and how the microstructural features control the density, mechanical properties thermal conductivity and other thermophysical properties of the fibers will be established.

Predictive models are being developed to relate the response of a carbon-carbon nozzle or nosetip in a given environment to microstructure. The value of these models contributing to material improvement is limited because the fundamental understanding between in-process events and microstructure is lacking. Microstructure is the link between processing and performance with process chemistry of the matrix being the key to controlled carbon microstructural development. Plans include the investigation of the polymerization, mesophase development, decomposition, carbonization, graphitization, densification, microstructural development, and microstructure/thermophysical property relationships in the carbon-carbon composites.

Air Force Research in Molecular Dynamics

Lt Colonel J. T. Viola

Air Force Research in Molecular Dynamics: A useful definition of molecular dynamics is obtained from R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics; "the subject of molecular dynamics deals with the study of the molecular mechanism of elementary physical and chemical rate processes. It is concerned with both intramolecular motions and intermolecular collisions, which together constitute the underlying 'microscopic' basis of all bulk rate phenomena". Michael Berry's definitions in "Laser Studies of Gas Phase Chemical Reaction Dynamics" in Annual Review of Physical Chemistry, 26, 259 (1975) is also a good working definition.

The Air Force Office of Scientific Research (AFOSR) has helped to foster growth in this area of science. It has recognized the need for the enhancement of understanding in this field and has sought to bring it to bear on Air Force problems.

What Air Force interests can be served by increased understanding of microscopic rate processes? To answer this question requires an understanding of the mission of the Air Force to help defend our American way of life. It accomplishes this mission by maintaining the capability to defend not only the air space contiguous to our territories and possessions but also that of other states who look to us to help protect their interests. Therefore, the Air Force must have a capability to carry out operations consistent with its mission. These operations naturally include a capability to communicate by means of electromagnetic signals that must propagate through a benign or disturbed atmosphere; it must be capable of detecting and discriminating weapons systems through analysis of emission characteristics; and it must employ the most sophisticated and advanced weaponry that our technology can produce. It is in these three areas, namely atmospheric processes as they affect communications; hostile weapon system emissive properties and electromagnetic weaponry that the study of molecular dynamics makes its greatest and most effective contributions.

Thus, studies of physical and chemical processes that occur in the atmosphere, such as ion-molecule reactions, photofragmentation, etc., are pursued to increase our understanding of the behavior of the atmosphere under "normal" conditions which include auroral phenomena. Studies are also undertaken to determine the effects of perturbations on the atmosphere. These may include the interactions produced by a nuclear burst or a missile plume or wake. This kind of information is needed to increase our probability of keeping "open" our communication channels as well as to detect and discriminate hostile exhaust emissions in an ever changing background of radiation. Molecular dynamics also provides important new information that is useful in the development of efficient, high energy, chemically pumped lasers. The familiar gas dynamic laser is a "chemical" laser of a certain kind in that the CO_2 lasing molecules are pumped by vibrational energy transfer. We consider non-reactive, but inelastic collisions such as vibrational to vibrational, vibrational to electronic (V-V, V-E), etc., energy transfer as an important part of molecular dynamics so lasers pumped in this fashion come within our purview.

We are most interested in lasers that are pumped directly by the energy released from an exoergic chemical reaction such as the HF or DF laser produced in the chemical reactions of fluorine with hydrogen (deuterium); and in processes in which energy as vibration or electronic, initially produced by exoergic chemical reactions, is transferred to another molecule which then lases. An illustration of the latter is the pumping of the CO_2 laser by energy transfer from the excited products of the exoergic chemical reaction of magnesium with oxygen.

The main thrust of research in this area is toward the development of high energy, efficient, chemically pumped lasers of shorter wavelength, below two micrometers. We know that laser light in wavelengths toward the visible region of the spectrum propagate more efficiently through the atmosphere. In addition, the energy per photon increases with frequency of the photon ($E = h\nu$); simplistically for a given weight of fuel that produces say one photon of laser light per chemical reaction, more energy is available in the laser beam for shorter wavelength transitions. The achievement of a short wavelength, chemically pumped, is seemingly difficult and fraught with many facts of nature which frustrate our most active attempts. Lasers operating in the visible region of the spectrum require the selective excitation of an electronically excited energy level whose radiative lifetime is sufficiently long (10^{-5} seconds) such that mixing times for the reagents are not rate limiting. This is a tall order and one that has not yet been achieved. There are promising candidate molecules such as SnO , SiF , ScF , YCl , yet much work is yet to be done to characterize reaction rates, lifetimes, branching ratios, and spectroscopy of these molecules. We intend to pursue these studies.

An important development that became effective on 1 July 1975 was the centralization of all Air Force basic research under a single manager - the Director of AFOSR. In addition to grants and contracts that are administered by AFOSR in Washington, D.C., there is an in-house, Air Force Laboratory program of research. A goal has been established of a 70 to 30 ratio of extramural research to in-house research. The extramural portion can be administered by the laboratories as well as by AFOSR Washington. An important result of this reorganization is a closer tie of the "Washington" research program to Air Force needs. Air Force laboratories that perform research in areas related to Molecular Dynamics include the Air Force Geophysics Lab at Hanscom AFB, Massachusetts, the Air Force Weapons Lab, Kirtland AFB, New Mexico, and the AF Rocket Propulsion Lab at Edwards AFB, California. Other areas of research in chemistry are performed at these and other laboratories.

The wisdom of this reorganization is evident when one realizes that the Air Force Laboratories provide the link from the basic research to the development of the final product. The chain thus runs from our universities, institutions and industry through AFOSR and the AF laboratories to the Air Force Product Divisions and finally to the operational commands.

FY 75 CHEMISTRY PROGRAM STATISTICS

(1 July 1974 to 30 June 1975)

	<u>Number</u>
New Work Efforts	23
Renewal Efforts	56
Completed Efforts	41
Number of Active Efforts (as of 30 June 1975)	90
FY75 Monies Committed	\$3,213K

PROPOSAL ACTION

New Proposals Received	163
New Proposals Declined or Withdrawn	140
New Proposals Funded in FY75	23

FY76 CHEMISTRY PROGRAM STATISTICS

(1 July 1975 - 30 June 1976)

	<u>Number</u>
New Work Efforts	32
Renewal Efforts	53
Completed Efforts	28
Number of Active Efforts (as of 30 June 1976)	84
FY-1976 Monies Committed	\$3,620K

PROPOSAL ACTION

New Proposals Received	221
New Proposals Declined or Withdrawn	185
New Proposals Funded in FY76	36

CHEMISTRY ANNUAL BUDGET FOR PAST TEN YEARS

<u>FY</u>	<u>Expenditures (thousands)</u>
67	\$3,480
68	3,329
69	3,338
70	3,169
71	3,205
72	3,210
73	2,512
74	3,080
75	3,213*
76	3,620

* FY-75 total includes \$570,449 from Project 9750 for Kinetics and Thermo-physical Properties Research.

SYMPOSIA

The support of symposia is an important part of activities by the Directorate of Chemical Sciences to publicize and stimulate areas of interest to the Air Force. The following list includes symposia sponsored by the Directorate during FY75-76:

AFML/AFOSR Workshop on the Role of the Polymer Substrate
Interphase in Structural Adhesion.

Dr. L. T. Drzal
Contract F33615-76-M-5452
University of Dayton
Dayton, Ohio
9-10 September 1976

AFOSR Workshop on the Effects of Relative Humidity and
Elevated Temperatures on Composite Structures.

Dr. J. R. Vinson and Dr. R. B. Pipes
AFOSR-76-2966
University of Delaware
Newark, Delaware
30-31 March 1976

(co-sponsored with AFOSR Directorate of Aerospace Sciences)

Corrosion Prevention Workshop.

Dr. Michael Hoch
AFOSR-PD-76-0003
University of Cincinnati
Cincinnati, Ohio
17-18 September 1975

Fourth Conference on Chemical and Molecular Lasers.

Dr. D. P. Ames
AFOSR-74-2740
Stouffer's Riverfront Inn
St. Louis, Missouri
21-23 October 1974

International Symposium on Macromolecules.

Dr. E. Banks
AFOSR-2829-75
New York City Community College
Brooklyn, New York
2-3 May 1975

Gordon Conference on Electrochemistry.

Dr. M. Brieter
AFOSR-75-2801
Maramar Hotel, Santa Barbara, California
January 1975

SYMPOSIA (continued)

Gordon Research Conference on Glass.

Dr. S. M. Ohlberg
AFOSR-76-3048
Plymouth State College
Plymouth, New Hampshire
2-6 August 1976

Gordon Research Conference on Inorganic Chemistry.

Dr. F. E. Brinckman
MIPR-0008-75
New Hampton School
New Hampton, New Hampshire
4-8 August 1975

Gordon Conference on Electrochemistry.

Dr. R. DeLevie
AFOSR-MIRP-76-0014
Maramar Hotel, Santa Barbara, California
19-23 January 1976

Second Summer Colloquium on Electronic Transition Lasers.

Dr. J. I. Steinfeld
AFOSR-2826
Conference Center
Marine Biology Institute
Woods Hole, Massachusetts
17-19 September 1975

Sixth International Liquid Crystal Conference.

Dr. A. DeVries and Dr. W. E. Bacon
AFOSR-76-3016
Kent State University
Kent, Ohio
23-27 August 1976

Second International Summer Institute in Surface Science.

Dr. Rolf Vanselow
MIPR-75-0011
University of Wisconsin - Milwaukee Campus
Milwaukee, Wisconsin
18-22 August 1975

Third Summer Colloquium on Electronic Transition Lasers.

Dr. J. I. Steinfeld
Wildwood Condominium Conference Center
Snowmass-In-Aspen, Colorado
7-10 September 1976

Symposium on Electrocatalysis - Electrochemical Society

Dr. M. Breiter
MIPR-74-0003
San Francisco, California
12-17 May 1974

Research Efforts (as of 30 June 1975)

ALPHABETICAL BY PRINCIPAL INVESTIGATOR

International Symposium on Macromolecules	Ephraim Banks Department of Chemistry Polytechnic Institute of New York Brooklyn, New York 11201
Visible Wavelength Chemiluminescence Initiated by Carbon Dioxide Laser Radiation	Simon H. Bauer Department of Chemistry Cornell University Ithaca, New York 14850
Chemical Laser Studies of Chemical Reaction Dynamics	Michael J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Molecular Electronic Photodissociation Laser Studies	Michael J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
1975 Gordon Research Conference on Inorganic Chemistry	F. E. Brinckman U.S. Department of Commerce National Bureau of Standards Washington, DC 20234
Spectroscopic and Kinetic Studies of Gas Phase Reactions	Herbert P. Broida Department of Physics University of California Santa Barbara, California 94110
Inelastic and Reactive Collisions of Translationally Excited Molecules	Philip R. Brooks Department of Chemistry Rice University Houston, Texas 77001
Electrochemistry of Hydrazine-Hydrazine Azide Mixtures	Charles T. Brown United Aircraft Research Laboratories United Technologies Corporation East Hartford, Connecticut 06108
Solid Electrode Studies Related to Corrosion Prevention, Fuel Cells, and Batteries	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York 14214
Kinetics of Association-Dissociation Reactions and Energy Transfer in Diatomic Molecules	George Burns Department of Chemistry University of Toronto Toronto, CANADA M5S 1A1
Energy Transfer and Chemical Reactions Important in Molecular Lasers	George Burns Department of Chemistry University of Toronto Toronto, CANADA M5S 1A1

Viscosity Measurements and Lubricating
Quality of Lubricants with Thickeners at
High Temperatures

Kinetics Studies Involving Electronically-
Excited Interhalogens and Halogens

Novel Chemical Laser Systems

Luminescent Transition Metal Complexes
in Magnetic and Electric Fields

Energy Migration Involving Irradiated
Solids

Chemical Reactions that Produce Electron-
ically Excited Metal Atoms

Development of Practical MO Techniques
for Prediction of the Properties and
Behavior of Materials

Evaluation of Chemical Research Relevant
to Current and Projected U.S. Air Force
Interests

Semiconductor Surface Chemistry

Rates of Rapid Chemical Reactions

Molecular Beam Investigation of Energy
Transfer and Chemical Reactivity

Alastair Cameron
College of Science and Technology
Imperial College
London, SW7, ENGLAND

M. A. A. Clyne
Department of Chemistry
Queen Mary College
London E1 4NS, ENGLAND

Terrill A. Cool
College of Engineering
Cornell University
Ithaca, New York 14850

Glenn A. Crosby
Department of Chemistry
Washington State University
Pullman, Washington 99163

J. Cunningham
University College of Cork
Cork, IRELAND

Paul Davidovits
Department of Chemistry
Boston College
Chestnut Hill, Massachusetts 02167

Michael J. S. Dewar
Department of Chemistry
University of Texas
Austin, Texas 78712

Joseph E. Earley
Department of Chemistry
Georgetown University
Washington, DC 20057

Gert Ehrlich
Coordinated Science Laboratory
University of Illinois
Urbana, Illinois 61801

Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

John B. Fenn
Department of Engineering
and Applied Science
Yale University
New Haven, Connecticut 06520

The Structure and Properties of Polymeric
Materials

Paul J. Flory
Department of Chemistry
Stanford University
Stanford, California 94305

Theoretical and Computational Studies of
Electronic Transitions in Molecular
Collisions

Thomas F. George
Department of Chemistry
University of Rochester
Rochester, New York 14627

Ionization Processes Relevant to the
Formation of New Materials

Harlan L. Goering
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Absolute Rate Constants for Combustion
Reactions Involving Free Radicals

D. M. Golden & S. W. Benson
Stanford Research Institute
Menlo Park, California 94025

Plastic Crystals as Model Substances for
Glasses

Martin Goldstein
Belfer Graduate School of Science
Yeshiva University
New York, New York 10033

Synthesis and Polymerization of Fluoro-
bicyclobutanes to Chemically, Thermally
and Dimensionally Stable Polymers

H. K. Hall, Jr.
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Photoluminescence Spectroscopy of Diatomic
Metal Oxides and Halides

David O. Harris
Department of Chemistry
University of California
Santa Barbara, California 93106

Investigation of the Synthesis and the
Related Microstructures and Properties
of Alloy Systems

Michael Hoch
Metallurgy and Material Sciences
University of Cincinnati
Cincinnati, Ohio 45221

Mechanisms of Singlet Oxygen Generation
by Chemical Reaction

James K. Hurst
Department of Chemistry
Oregon Graduate Center
Beaverton, Oregon 97005

High-Pressure Nuclear Magnetic Resonance
Relaxation Study of Supercritical Dense
Fluids

Jiri Jonas
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Effect of Structure on the Physical
Properties of Polymers

Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002

Computer Modeling of Pulsed Chemical
Lasers

Ronald L. Kerber
Department of Mechanical
Engineering
Michigan State University
East Lansing, Michigan 48824

- | | |
|---|--|
| Novel Organophosphorus and Organonitrogen Derivatives and Their Use for the Synthesis of Unusual Transition Metal Complexes | R. Bruce King
Department of Chemistry
University of Georgia
Athens, Georgia 30601 |
| Theories of Energy Disposal in Chemical Reactions | Aron Kuppermann
Division of Chemistry and
Chemical Engineering
California Institute of Technology
Pasadena, California 91109 |
| Synthesis of Organofluorine Compounds by Direct Fluorination | Richard Lagow
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 |
| Infrared Spectra of Fluid Films Under Conditions of Incipient Bearing Failure | James L. Lauer
Applied Research Department
Sun Oil Company
P.O. Box 1135
Marcus Hook, Pennsylvania 19061 |
| Energy and Chemical Change | R. D. Levine and R. Bernstein
Department of Chemistry
University of Texas
Austin, Texas 78712 |
| Structure and Properties of Glasses | Pedro B. Macedo & T. A. Litovitz
Department of Physics
Catholic University of America
Washington, DC 20017 |
| Structure and Properties of Glasses | John D. Mackenzie
Department of Chemistry
University of California
Los Angeles, California 90024 |
| Molecular Basis for Liquid Crystal Field Effects | J. David Margerum
Photochemistry Section
Hughes Research Laboratories
Malibu, California 90265 |
| Studies of Laser-Induced Photochemical Kinetics | R. A. McFarlane
School of Electrical Engineering
Cornell University
Ithaca, New York 14850 |
| Lasing from the Combustion of Unusual and Labile Species | Henry A. McGee, Jr.
Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, Virginia 24061 |
| The Reactivity and Structure of Solid Surfaces | Robert P. Merrill
Department of Chemical Engineering
University of California
Berkeley, California 94720 |

Calculation of Potential Energy Surfaces &
Collision Cross Sections

Harvey H. Michels
United Aircraft Research Laboratories
United Technologies Corporation
East Hartford, Connecticut 06108

Electrochemical Studies in Aluminum
Chloride Melts

Robert A. Osteryoung
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80521

Chemical Lasers, Ultrarapid Scan Infrared
Studies & Laser-Induced Kinetic
Processes

George C. Pimentel
Department of Chemistry
University of California
Berkeley, California 94720

Experimental and Theoretical Studies in
Photochemistry

Stuart A. Rice
Department of Chemistry
University of Chicago
Chicago, Illinois 60637

High Energy Chemical Reactivity

John W. Root
Department of Chemistry
University of California
Davis, California 95616

Molecular Beam Studies of Ionization
Processes

Erhard W. Rothe
Department of Chemical Engineering
Wayne State University
Detroit, Michigan 48202

Highly Halogenated Organic and Organo-
metallic Materials and Strained Ring
Organometallics

Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Molecular Energy Transfer by Collisional
Processes Characteristic of Gas Lasers

Hyung Kyu Shin
Department of Chemistry
University of Nevada
Reno, Nevada 89507

Reactive Atomic Species Generated at
High Temperatures and Their Low
Temperature Reactions to Form Novel
Substances

P. S. Skell
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Photochemical Addition of Benzene to
Unsaturated Materials

Ringaswamy Srinivasan
IBM Corporation
T. J. Watson Research Center
Yorktown Heights, New York 10598

Molecular Behavior Studies of Glassy
Polymers Under Stress

W. O. Statton
College of Engineering
University of Utah
Salt Lake City, Utah 84112

Formation and Deactivation Processes in
Electronic Transition, Chemically
Pumped Lasers

J. I. Steinfeld & J. L. Gole
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

2nd Summer Colloquium on Electronic
Transition Lasers

J. I. Steinfeld & J. L. Gole
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Transition Metal Compounds with Potential
Electronic and Radiation Resistant
Properties

F. G. A. Stone
Department of Chemistry
University of Bristol
Bristol, ENGLAND

Collisional Excitation of Radiative
Vibrational Modes in Some Simple
Polyatomic Molecules

R. B. Subbarao & J. B. Fenn
Department of Engineering Sciences
Yale University
New Haven, Connecticut 06520

Chemical Kinetics of Some Elementary
Reactions of Oxygen Atoms

R. B. Timmons
Department of Chemistry
Catholic University of America
Washington, DC 20017

Structural and Dynamic Studies of
Materials Possessing High Energy
Content

Nicholas J. Turro
Department of Chemistry
Columbia University
New York, New York 10027

The Second International Summer Institute
in Surface Science

Ralf Vanselow
Department of Chemistry
University of Wisconsin
Milwaukee, Wisconsin 53201

Applied Quantum Chemistry of Nonmetallic
Materials

John R. Van Wazer
Department of Chemistry
Vanderbilt University
Nashville, Tennessee 37203

Unsaturated Organosilicon Heterocycles

W. P. Weber
Department of Chemistry
University of Southern California
Los Angeles, California 90007

Structure and Properties of High
Temperature Materials

William Weltner, Jr.
Department of Chemistry
University of Florida
Gainesville, Florida 32611

Chemical Reactions and Properties of
Organosilicon Compounds Related to
New Materials

Robert C. West
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Studies of Rotationally Cooled Molecules
in Molecular Beams by Laser Spectroscopic
Technique

L. Wharton
Department of Chemistry
University of Chicago
Chicago, Illinois 60637

Energies and Conformations of Molecules

Kenneth Wiberg
Department of Chemistry
Yale University
New Haven, Connecticut 06520

Electrode Mechanisms Using Reflection
and Electron Spectroscopy

Nicholas Winograd
Department of Chemistry
Purdue Research Foundation
Lafayette, Indiana 47907

Internal State Identification of Reaction
Products

R. N. Zare
Department of Chemistry
Columbia University
New York, New York 10027

Research Efforts Completed in FY75

(Alphabetical by Principal Investigator)

Adsorption on Molecular Solids	Arthur W. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007
Fourth Conference on Chemical and Molecular Lasers	D. P. Ames Conference on Chemical and Molecular Lasers, Inc. c/o McDonnell-Douglas Corporation P.O. Box 516 St. Louis, Missouri 63166
Combustion Analysis and Chemistry of Flames	Kyle D. Bayes Department of Chemistry University of California Los Angeles, California 90024
Microwave Spectroscopy of Boron Compounds Related to High Temperature Polymers	Robert A. Beaudet Department of Chemistry University of Southern California Los Angeles, California 90007
Reactions and Electrochemical Kinetics of Newly Generated Metal Surfaces	T. R. Beck Flow Research, Inc. 1819 S. Central Ave. Suite 72 Kent, Washington 98031
The Chemistry of Photographic Systems and Reactions	George R. Bird Department of Chemistry Rutgers University New Brunswick, New Jersey 08903
Stabilized Detonation on Wave Chemical Laser Systems	J. R. Bowen Department of Chemical Engineering University of Wisconsin Madison, Wisconsin 53706
Spectroscopic Studies of Energy Exchange Processes	H. P. Broida Department of Physics University of California Santa Barbara, California 93106
Prediction of Properties and Behavior of Materials	Michael J. S. Dewar Department of Chemistry University of Texas Austin, Texas 78712
Reactivity Patterns Characteristic of Lighter Metallic Elements (Titanium)	Joseph E. Earley Department of Chemistry Georgetown University Washington, DC 20007

Chemical Reactions Induced by Ultraviolet
and Ionizing Radiation

George S. Hammond
Department of Chemistry
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University of California (Santa Cruz)
Santa Cruz, California 95060

Electronically Excited Metal Atoms
Produced by Chemical Reactions

J. L. Hirschfield
Department of Engineering and
Applied Science
Yale University
New Haven, Connecticut 06520

Non-Stoichiometric Oxides: Structure,
Texture, Thermodynamics and Magnetic
Properties

Bruce G. Hyde and B. N. Figgis
Department of Chemistry
University of Western Australia
Nedland, WESTERN AUSTRALIA 6009

The Solid-State Properties of Transition
Metal Complexes

Leonard V. Interrante
Physical Chemistry Laboratory
General Electric Company
Research & Development Center
Schenectady, New York 12301

Collisional Energy Transfer and Other
Topics Related to Gas Laser Mechanisms

Ali Javan
Department of Physics
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Transition Metal and Lanthanide Compounds

R. B. King
Department of Chemistry
University of Georgia
Athens, Georgia 30602

Inorganic Photoelectron Spectroscopy,
Mass Spectrometry, and Thermochemistry
Related to Fuels and Polymers

M. F. Lappert & J. B. Pedley
Department of Chemistry
University of Sussex
Brighton BN1 9QJ
Sussex, ENGLAND

Chemical Kinetics of Selected Fluorine
Reactions

J. B. Levy
Department of Chemistry
The George Washington University
Washington, DC 20052

Structure and Properties of Glasses

John D. Mackenzie
Department of Chemistry
University of California
Los Angeles, California 90024

Fast Kinetic Methods Applicable to Trace
Chemical Analysis and Detection

Dale W. Margerum & Harry L. Pardue
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Quantum Theoretical Studies of Gas-Solid Interactions

R. P. Messmer
Physical Chemistry Laboratory
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Influence of Collision Cross-Sections for Electrons, Atoms and Molecular Systems

Harvey H. Michels
United Technologies Research Center
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Calculations of Electronic Wave Functions

Harvey H. Michels
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Electronic and Magnetic Properties of High Temperature Electrolytes

Norman H. Nachtrieb
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5801 Ellis Ave
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Synthesis and Properties of Rotaxane Compounds

Melvin S. Newman
Department of Chemistry
Ohio State University
Research Foundation
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Electrochemical Studies in Aluminum Chloride Melts

Robert A. Osteryoung
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

Gas Phase Reactions of Atoms, Ions and Simple Molecules Related to Upper Atmosphere Chemistry

Leon F. Phillips
Chemistry Department
University of Canterbury
Christchurch, NEW ZEALAND

Properties of Selected Chemical Compounds for Preparation of New Materials

Michael T. Pope
Department of Chemistry
Georgetown University
Washington, DC 20007

Molecular Beam Methods of Evaluating High Energy Sources for Advanced Propulsion Systems

E. W. Rothe
Research Institute for
Engineering Sciences
College of Engineering
Wayne State University
Detroit, Michigan 48202

Energy Transfer Processes in Gas Laser Materials

D. J. Seery
United Technologies Research Center
East Hartford, Connecticut 06108

Properties and Reactions of Atomic Species Generated at High Temperatures

P. S. Skell
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Molecular Processes Controlling Energy Transfer

E. W. Schlag
Institute for Physical Chemistry
Technical University, Munich
Munich, Germany

Absorption and Collisional Redistribution of Molecular Energy Revealed by Double Resonance Spectroscopy/Molecular Deactivation Processes in Visible Chemical Laser Systems

J. I. Steinfeld
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Solute-Solvent Interactions and Preferential Solvation: An NMR Study

Thomas R. Stengle
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

New Perfluoropolymer-Forming Reactions

Madeleine S. Toy
Stanford Research Institute
Menlo Park, California 94025

Organolanthanides and Organoactinides Related to Catalysis

Minoru Tsutsui
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Structure and Properties of High Temperature Species Related to Ablative Re-Entry and Solid Propellants

William Weltner, Jr.
Department of Chemistry
University of Florida
Gainesville, Florida 32611

Analysis of the Collisional Redistribution of Molecular Energy in Gases

Lennard Wharton
James Franck Institute and
Department of Chemistry
University of Chicago
Chicago, Illinois 60637

Completed Project Summaries

FY-75

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COMPLETED PROJECT SUMMARY

1. TITLE: Absorption on Molecular Solids
2. PRINCIPAL INVESTIGATOR: Professor A. W. Adamson
Department of Chemistry
University of Southern California
Los Angeles, California 90007
3. INCLUSIVE DATES: 1 January 1971 - 31 August 1974
4. GRANT NUMBER: AFOSR-71-2029
5. COST AND FY SOURCE: \$42,000 FY71; \$21,000 FY73
6. SENIOR RESEARCH PERSONNEL: M. Tadros
S. Levine
L. Dormant
7. JUNIOR RESEARCH PERSONNEL: B. Jones J. Tse
F. Shirley M. Beverly
P. Hu S. Cutri

8. PUBLICATIONS:

"Physical Adsorption of Vapors on Ice. IV. Carbon Dioxide", A. W. Adamson and B. R. Jones, J. Colloid and Interface Sci., **37**, 831 (1971).

"Application of the BET Equation to Heterogeneous Surfaces", L. M. Dormat and A. W. Adamson, J. Colloid and Interface Science, **38**, 285 (1972).

"Potential Distortion Model for Contact Angle and Spreading II. Temperature Dependent Effects", A. W. Adamson, J. Colloid and Interface Sci., **44**, 273 (1973).

"Adsorption and Contact Angle Studies I. Water on Smooth Carbon, Linear Polyethylene, and Stearic Acid-Coated Copper", M. E. Tadros, P. Hu, and A. W. Adamson, J. Colloid and Interface Sci., **49**, 184 (1974).

9. ABSTRACT OF ACCOMPLISHMENTS AND OBJECTIVES:

This research was oriented towards the characterization of the interface between a molecular solid and a liquid or vapor phase. Emphasis was on interface structure and structural changes accompanying absorption. The studies included vapor absorption on ice, liquid interface, and absorption at the interface between a molecular solid and solution. Measurements were made of absorption layer thickness, contact angles, heats of absorption, and entropy of absorption. The goal was to substantiate a generalization for interfacial behavior, thereby permitting the prediction of surface characteristics and restrictions.

In the contact angles on molecular solid study the interest was on the wetting behavior of various liquids with respect to ice, including temperature dependence. A concept was derived of an A and B class system, the distinction being the degree of restructuring of the ice that occurs on contact with the liquid phase. Class A systems, with little restructuring, should exhibit weaker adhesion and thus are of interest in de-icing problems.

In the physical adsorption area, results show that above - 350°C ice surface is restructured by hydrocarbon adsorbents, but below this temperature the surface is rigid.

A model was developed which allows calculation of contact angle and wetting behavior from adsorption isotherms alone. The model unifies what has been two separate fields.

An ellipsometric method was used to measure water vapor on polyethylene and various pyrolytic carbon surfaces. The data of adsorption and contact angle of liquid water on the same surface were related by means of the adsorption model.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Fourth Conference on Chemical and Molecular Lasers
2. PRINCIPAL INVESTIGATOR: Dr. D. P. Ames
Conference on Chemical and Molecular Lasers, Inc.
c/o McDonnell-Douglas Corporation
P.O. Box 516
St. Louis, Missouri 63166
3. INCLUSIVE DATES: 1 June 1974 to 31 May 1975
4. GRANT NUMBER: AFOSR-74-2740
5. COST AND FY SOURCE: \$5,000 FY 74
6. RESEARCH PERSONNEL: Dr. D. P. Ames
7. PUBLICATIONS:

Seven publications in J. Quantum Electronics QE-11, 641-723 (1975).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of the Conference were to bring people together active in research in chemical and molecular lasers, to present recent research results and to encourage the exchange of ideas and discussions of the state of the art. Topics included results on laser reactions, search for new chemical laser reactions, refinement of the theory and modeling of the systems, collisional relaxation phenomena, initiation techniques, electron beam pumped lasers, and laser controlled chemistry.

The Fourth Conference on Chemical and Molecular Lasers was held 21-23 October 1974 at Stouffer's Riverfront Inn, 200 South Fourth Street, St. Louis, Missouri 63102. Two hundred forty people registered at this conference. In addition to the 86 papers abstracted in the Digest, 20 postdeadline papers were included in two sessions. Professor Melvin B. Gottlieb presented the Banquet address to 104 Conference participants.

Eight full-length papers were submitted for publication in the special issue of Journal of Quantum Electronics. Seven papers were passed by referees sanctioned by the journal editor and were published along with the Digest of Technical Papers (includes abstracts of the postdeadline papers) in J. Quantum Electronics QE-11, 641-723 (1975).

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Combustion Analysis and Chemistry of Flames
2. PRINCIPAL INVESTIGATOR: Dr. Kyle D. Bayes
Department of Chemistry
University of California
Los Angeles, California 90024
3. INCLUSIVE DATES: 15 October 1969 to 14 October 1974
4. GRANT NUMBER: AFOSR-70-1872
5. COSTS AND FY SOURCE: \$31,656 FY 70; \$24,965 FY 71
\$53,024 FY 72
6. SENIOR RESEARCH PERSONNEL: Dr. I. T. N. Jones
Dr. C. Vinckier
Dr. N. Washida
Dr. D. G. Williamson
7. JUNIOR RESEARCH PERSONNEL: M. Gardner
R. Martinez
8. PUBLICATIONS:

"The Reaction of $O(^3P)$ with Dideuterioacetylene," D. G. Williamson, J. Phys. Chem. 75, 4053 (1971).

"Electronic Energy Transfer from $^{32}O_2(a^1\Delta_g)$ to $^{36}O_2(X^3\Sigma_g)$," I. T. N. Jones and K. D. Bayes, J. Chem. Phys. 57, 1003 (1972).

"Detection of Steady-State Free-Radical Concentrations by Photo-ionization," I. T. N. Jones and K. D. Bayes, J. Am. Chem. Soc. 94, 6869 (1972).

"Free Radical Formation in the $O + C_2H_2$ Reaction," I. T. N. Jones and K. D. Bayes, 14th Symposium on Combustion, pg. 277 (1972).

"Formation of $O_2(a^1\Delta_g)$ by Electronic Energy Transfer in Mixtures of NO_2 and O_2 ," I. T. N. Jones and K. D. Bayes, J. Chem. Phys. 59, 3119 (1973).

"Photolysis of Nitrogen Dioxide," I. T. N. Jones and K. D. Bayes, J. Chem. Phys. 59, 4836 (1973).

"The Rate of Reaction of Methyl Radicals with Atomic Oxygen," N. Washida and K. D. Bayes, Chem. Phys. Ltrs. 23, 373 (1973).

"The Kinetics and Mechanism of the Reaction of Atomic Oxygen with Acetylene," I. T. N. Jones and K. D. Bayes, Proc. Roy. Soc. Lond. A335, 547 (1973).

"The Oxidation of Formyl Radicals," N. Washida and K. D. Bayes, Z. Naturforsch. 29a, 251 (1974).

"Gas Phase Ozone-Olefin Reactions: Part I Low Pressure Chemiluminescence and Kinetics" by B. J. Finlayson, J. N. Pitts, Jr. and R. Atkinson, J. Am. Chem. Soc. 95, 7592 (1973). This work was done by the University of California, Riverside group using the UCLA photoionization mass spectrometer; an acknowledgement to AFOSR is given at the end of the paper.

"Identification of the Primary Chemi-ion in Hydrocarbon Oxidations," M. P. Gardner, C. Vinckier and K. D. Bayes, submitted to Chem. Phys. Ltrs.

"The Oxidation of Methyl Radicals," N. Washida and K. D. Bayes, manuscript in preparation.

"The Oxidation of Isobutane and the Tertiary Butyl Radical," N. Washida and K. D. Bayes, manuscript in preparation.

"The Oxidation of Acetaldehyde and the Acetyl Radical," N. Washida and K. D. Bayes, manuscript in preparation.

"The Oxidation of Propane and the Propyl Radical," N. Washida, manuscript in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An important new analytical instrument, the photoionization mass spectrometer, has been constructed, tested, and used to investigate the rates and mechanisms of several gas phase reactions. Photoionization makes it possible to very selectively ionize free radicals, electronically excited molecules, or other species having low ionization potentials. For the first time it has been possible to observe a great variety of hydrocarbon free radicals at their steady state concentrations in low pressure flames. Two new free radicals have been discovered (C_3H_3 , HC_2O) and several free radicals, known previously only by spectroscopic observations, have been studied kinetically. The reaction between oxygen atoms and acetylene has been studied extensively; it has been shown that there are three competing channels in the initial reaction, rather than only one as thought previously. The direct observation of free radicals has led to a new technique of measuring very fast rate constants, the approach to steady state method. Using this technique, five new rate constants have been measured for reactions that occur on almost every collision. The reaction of several hydrocarbon free radicals with molecular oxygen has been explored. The reaction of methyl radicals with O_2 , which is an important reaction in the stratosphere, as well as in ordinary combustion, has been shown to involve both two-body and three-body mechanisms, and the two rate constants show different temperature dependences.

It has been proven that CHO^+ is the primary chemi-ion formed in hydrocarbon flames. By using a special reactor and applying a radical electric field, it was possible to extract the primary chemi-ion before ion-molecule reactions concealed its identity. The rate constants for several ion-molecule reactions are being measured using this same reactor.

The absorption of light by NO_2 is an important process both in the stratosphere and in polluted urban air. The quantum yield for

photodissociation has been measured as a function of wavelength. The behavior of the quantum yield in the neighborhood of the dissociation limit (398 nm) is not in accord with previous theories of photodissociation, and as of now is still unexplained. In the visible part of the spectrum, where NO_2 cannot photodissociate, it was discovered that the electronically excited NO_2 could transfer its energy to molecular oxygen to form metastable O_2 (singlet oxygen).

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Microwave Spectroscopy of Boron Compounds Related to High Temperature Polymers.
2. PRINCIPAL INVESTIGATOR: Dr. Robert A. Beaudet
Department of Chemistry
University of Southern California
Los Angeles, California 90007
3. INCLUSIVE DATES: 1 November 1971 - 31 October 1974
4. GRANT NUMBER: AFOSR-72-2157
5. COSTS AND FY SOURCE: \$30,271 FY72; \$29,608 FY73
6. SENIOR RESEARCH PERSONNEL: G. J. McKown
J. P. Pasinski
K. K. Lau
D. Russell
7. JUNIOR RESEARCH PERSONNEL: H. Rogers
B. Don
8. PUBLICATIONS:

"The Microwave Spectrum, Structure and Dipole Moment of N, N Dimethylaminodiborane", E. A. Cohen, Inorg. Chem. 12, 1570 (1973).

"Determining of Molecular Structure of $C_4B_2H_6$ by Microwave Spectroscopy", J. P. Pasinski, J. Chem. Soc., 928 (1973).

"Microwave Spectrum, Structure, and Dipole Moment of 2,3,4,5-Tetracarba-hexaborane (6)" J. P. Pasinski, J. Chem. Phys. 61, 683 (1974).

"Microwave Spectrum, Structure and Dipole Moment of Aminodiborane", K. K. Lau and A. B. Burg, Inorg. Chem. 13, 2787 (1974).

"Skeletal Molecular Structure of Monocarba-hexaborane (7) from Microwave Spectral Studies", G. L. McKown, B. P. Don, P. J. Vergamini and L. H. Jones, Chem. Comm., 765 (1974).

"Skeletal Molecular Structure of Monocarba-hexaborane (7) from Microwave Spectral Studies", G. L. McKown, B. P. Don, P. J. Vergamini and L. H. Jones, J. Chem. Soc. Chem. Commun. 19, 765-6 (Eng) (1974).

"Microwave Spectrum, Structure and Dipole Moment of 1,7-Dicarboclosooctaborane(8), $C_2B_6H_8$ ", K. K. Lau and N. H. Rogers, manuscript in preparation.
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The prime objective of this effort was to determine the geometries, accurate structures and related molecular properties and motions of carboranes and related compounds. The reasons for the studies were to understand the bonding which occurs in these interesting systems, understand the sites of reactivity and the reaction paths, and predict new families of compounds which should be stable and possibly indicate routes to their preparation.

The first efforts were devoted to the determination of the structures of closed polyhedrals. These studies were responsible for the determination and confirmation that small carboranes with the empirical formula $C_2B_nH_{n+2}$ all had closed polyhedral structures. In some instances the symmetries and the relative orientations of the atoms within the structure were known, while in others they were determined from this work. From the comparison of the NMR structures of known systems which this group studied, it has now been possible to determine the locations of boron atoms in new systems by comparing the known chemical shifts for given environments to those in the new unknown compounds.

The rotational spectrum of the boron isotopic species were all studied. The information was sufficient to confirm that the structure was a pentagonal bipyramid and to determine that the two carbons were in equatorial positions separated by one boron atom. Later the ^{13}C enriched isotopes were prepared by Professor Thomas Onak and Professor Jack Spielman at California State in Los Angeles. When the spectra of these isotopes were obtained, a complete skeletal structure was determined and subsequently published.

This work vividly illustrated that rotational spectroscopy could be used for the determination of the molecular structures of large volatile molecules. The structure of a new kind of compound was determined. From bond distances which were determined for the compound, it was inferred that carbon was bonded to five atoms and hence behaved in a "nonclassical" manner.

The spectra of 1, 2 dicarbahexaborane were determined. There are two stable geometric isomers of this compound. The asymmetric isomer has a dipole moment while the other has none by symmetry. From the NMR data it could be inferred that $C_2B_4H_6$ probably existed in an octahedral structure with two possible arrangements for the carbon, trans- and cis.

The first nido - compound to be studied was 2 carbahexaborane, originally prepared by Hawthorne and Dunks. The boron isotopic species of this compound was studied. From the investigation they were able to confirm (1) that the structure of this compound is a pentagonal pyramid with the carbon located in the base, (2) and to determine the boron-boron distances.

In order to test whether CNDO would be practicable for application with carboranes, CNDO investigations were undertaken of the closo-carboranes whose structures were known. Calculations were carried out on three possible isomers of $C_2H_5O_7$, the two isomers of $C_4B_2H_6$, and the four isomers of $C_2B_5H_7$. From these calculations it is concluded that CNDO method does seem accurate enough to predict rough trends and relative stabilities, charge densities and structures of carborane. They have also shown that there is little evidence the carboranes possess aromaticity.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Reactions and Electrochemical Kinetics of Freshly Generated Metal Surfaces.
2. PRINCIPAL INVESTIGATOR: Dr. Theodore R. Beck
Flow Research, Inc.
1819 South Central Avenue
Kent, Washington 98031
3. INCLUSIVE DATES: 1 December 1972 - 30 June 1975
4. CONTRACT NUMBER: F-44620-72-C-0070
5. COSTS AND FY SOURCE: \$41,251 FY72; \$48,249 FY73; \$27,969 FY74; \$44,997 FY75
6. SENIOR RESEARCH PERSONNEL: Mr. Steve Hanson
7. JUNIOR RESEARCH PERSONNEL: None.
8. PUBLICATIONS:

"One-Dimensional Pits in Titanium", presented at Electrochemical Society, Miami Beach, Florida, October 1972; published in J. Electro. Soc. 120, 1310 (1973).

"Electrochemistry of Freshly-Generated Titanium Surfaces, II", Electrochimica Acta, 18, 815 (1973).

"Electrochemical Reactions on Newly-Generated Titanium Surfaces", presented at NACE, Anaheim, California, March, 1973, published in Corrosion, 30, 408 (1974).

"Formation and Properties of Salt Films during Corrosion of Metals", presented at Electrochemical Society, Boston, Massachusetts, October 1973 (extended abstract in Appendix A).

"High-Current-Density Anodic Transients for Newly-Generated Titanium Surfaces", presented at NACE, Chicago, Illinois, March, 1974 (extended abstract in Appendix B, to be submitted to Corrosion).

"Electrical Transient Studies with One-Dimensional Pits in Titanium", presented at Gordon Conference on Corrosion, Colby College, New Hampshire, July, 1974 (work in progress, to be submitted to J. Electrochem. Soc.).

"Salt Films and Their Influence on the Corrosion of Metals", presented at NACE, Toronto, Canada, April, 1975 (extended abstract in Appendix C, to be submitted to Corrosion).

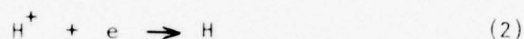
"The Occurance of Salt Films During Initial Stages of Titanium Corrosion", T. R. Beck, D. Ernsberger, and R. Alkire, to be presented at Electrochemical Society, Dallas, Texas, October 1975 (extended abstract in Appendix D, to be submitted to J. Electrochem. Soc.).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Air Force flight vehicles must withstand increasingly complex environmental and operational regimes. Fundamental knowledge of the mechanisms of fatigue and fracture of flight structures is required. This research is related to the understanding of crack propagation, stress corrosion and corrosion fatigue in titanium and other metals.

An electrochemical mass transport kinetic (MTK) model was previously formulated by the author to quantitatively describe the electrochemical events in a crack. It turned out that the model was not completely accurate because initial reactions on a newly-generated surface of titanium such as at the crack tip were not understood at that time. All electrochemical studies reported in the literature were for aged surfaces of titanium which had an oxide skin. The present work was done to fulfill the requirement of the model for quantitative data on new titanium surfaces and to develop a general understanding of the kinetics of the repassivation process.

Preliminary work had already shown that corrosion of the new metal surface is important as well as the hydrogen ion reduction and formation of oxide that were considered in the MTK model. All three reactions must be considered:



The first phase of experimentation was to generate current-time curves for new surfaces using 0.16 x 0.32 cm notched specimens and following the course of current versus time from generation (approx. 10^{-4} sec. from fracture) to steady state (approx. 10^4 sec.). The current density in this period decayed by a factor of 10^6 so that special instrumentation had to be built.

It became evident that reactions 1 and 2 dominated initially, giving a mixed potential at the surface. The measured initial anodic current of about $3\text{A}/\text{cm}^2$ was limited by iR drop in the electrolyte between the Luggin capillary and the new surface, and was obviously smaller than the true anodic current density. Because the initial reaction was considered to be important at the crack tip, it was necessary to design an experiment with lower ohmic resistance between the Luggin capillary and the specimen.

Notched 0.040 cm diameter wires were mounted in a Teflon holder with a Luggin capillary tip that approached within one wire diameter of the notch. This permitted initial current densities of over $10^2 \text{A}/\text{cm}^2$. Now some interesting new effects were observed. Passivation time was shorter at the higher initial current density, showing that it was due to an anodic process. Higher HCl concentration also caused a shorter passivation time, indicating a mass action effect on precipitation of a salt layer.

A review of the literature showed that after the classic researches of W. J. Muller in the 1920's and 30's on salt films in corrosion, the subject had been largely neglected. Experiments were therefore conducted with copper and silver at conditions at which salt films form but not oxides. Data were observed to fit the Sand equation for unsteady - state mass transport using degrees of supersaturation for the precipitating salt. Salt-film passivation times as short as milliseconds were observed for high dissolution current densities, directly analogous to experimental data for newly-generated titanium surfaces.

Studies were also made with pitting of titanium because in this case measurements can be made of the properties of the salt film at steady state. Conductivity and thickness were measured. An important observation made during pitting is that the metal-to-salt-film interface appears to be close to the equilibrium potential, even at high current density. It is proposed that a similar situation occurs at a crack tip and that the increase free energy there as a result of the stress intensity causes increased local activity and thus the crack to propagate.

A more fundamental model for salt film formation on newly-generated titanium surfaces is being formulated based on Fick's second law. When the salt film formation and dissolution are completely worked out, it is planned to revise the MTK model. Perhaps then the electrochemistry of crack propagation in titanium will be understood.

AFOSR Program Manager: R. W. Haffner, Lt Colonel

COMPLETED PROJECT SUMMARY

1. TITLE: The Chemistry of Photographic Systems and Reactions
2. PRINCIPAL INVESTIGATOR: Professor George R. Bird
School of Chemistry
Rutgers University
New Brunswick, New Jersey 08903
3. INCLUSIVE DATE: 16 January 1971 - 15 January 1975
4. GRANT NUMBER: AFOSR-71-2026
5. COSTS AND FY SOURCES: \$39,919 FY71; \$55,933 FY72
29,000 FY73; \$44,112 FY74
6. SENIOR RESEARCH PERSONNEL: Dr. V. A. Greenhut
Dr. J. K. Maurus
Dr. S. J. W. Platzer
7. JUNIOR RESEARCH PERSONNEL: J. Patenza W. D. Pandolphe
D. Mastropaolo A. Piechowski
W. Borowski L. Zyontz
A. Greenberg C. Reich
8. PUBLICATIONS:

"To any Interested Emulsion Maker, A Challenge", G. R. Bird, Photog. Sci and Eng., 15, 442 (1971).

"Circular Dichroism of Sensitizing Dye Aggregates", J. K. Maurus and G. R. Bird, J. Phys. Chem. 76, 2982 (1972).

"Note on a Dye Aggregate Structure Specific to the (100) Face of Silver Bromide", G. R. Bird, Photo. Sci. and Eng., 15, 134 (1971).

"Noiseless Chemical Amplifiers and the Ultimate Capabilities of Organic Imaging Systems", G. R. Bird, ibid., 17, 267 (1973).

"Attachments and Spectral Shifts of Dye Aggregates on Silver Bromide", C. Reich, W. D. Pandolfe and G. R. Bird, ibid., 17, 334 (1973).

"Chemisorbed Sensitizing Dye Aggregates with Herringbone Structure", C. Reich, ibid., 18, 335 (1974).

"Simultaneous Observations of Adsorption Isotherms and Absorption Spectra of Sensitizing Dyes on Single Crystals", W. D. Pandolfe and G. R. Bird, ibid., 18, 340 (1974).

"The Crystal and Molecular Structure of the Acetic Acid Solvate of 5,5'-Dichloro-9-Triethylthiacarbocyanine Bromide, a Photographic Sensitizing Dye", J. Potenza and D. Mastropaolo, Acta Cryst. B, 30, 2353 (1974).

"Overcoming and Limitation of Incomplete Absorption in Sensitization with Cyanine Dyes", G. R. Bird, ibid., 18, 562 (1974).

IN PREPARATION:

"The Problem of Instability and Fog in High Speed Organic Imaging Systems: Strategies for Improvement", W. D. Pandolfe and G. R. Bird.

"Crystal and Molecular Structure of 3,3'-Diethylthiatricarbocyanine Iodide", J. Potenza, L. Zyontz and W. Borowski.

"Transmission Electron Microscopic Investigation of Photographic Silver Iodobromide Crystals", S. J. W. Platzer and V. A. Greenhut.

"The Photoisomerization, Luminescence, and Sensitizing Action of Cyanine Dyes", A. Greenberg and G. R. Bird.

"The Supersensitization of AgBr Photoconductivity by Spectroscopically Degenerate Dye Pairs", A. Piechowski and G. R. Bird.

"New Methods for the Study of Adsorption Phenomena", G. R. Bird.

"The Circular Dichroism of Potentially Chiral Dyes Dispersed in a Chiral Matrix", W. D. Pandolfe and G. R. Bird.

"Polarized Light Absorption by Chemisorbed Dye Monolayers on Anisotropic Substrates", W. D. Pandolfe and G. R. Bird.

"Image Forming Reactions and Semitizing Dyes" FINAL REPORT - NDA-023053

9. ABSTRACT OF ACCOMPLISHMENTS AND OBJECTIVES:

This research was undertaken to generate new insights on the fundamental properties which limit the performance of chemical image-forming systems. The principal areas investigated were:

Dye sensitization of photoconductivity and of silver latent image formation.

The ultimate information-recording capabilities of organic imaging systems having chemical amplification, and strategies for overcoming problems of thermal instability in these systems.

Methods for simultaneously improving sensitivity and detection quantum efficiency of conventional silver halide photographic systems.

The following analyses and investigations were completed under the grant:

A complete theoretical and experimental analysis of the surface structures, packing geometries, and spectra of aggregates of some representative sensitizing dyes on the most common faces (111) and (100) of the silver halides for the case of red-shifted aggregate absorptions.

A theoretical and experimental analysis of the surface structures and spectra of dye aggregates having angled, "herringbone" packing geometries and giving broad, multi-peaked absorption bands corresponding to panchromatic sensitization of photographic materials.

Determination of the crystal structures of two critical cyanine dyes by X-ray diffraction.

Discovery of some "missing" aggregate structures and prediction of modified red sensitizing dyes which might take up these structures.

Measurement of the quantum yields of fluorescence and isomerization of some representative cyanines in fluid solutions at reduced temperature. Photo-isomerization is here established as a reaction competitive with dye sensitization.

Determination of the sensitized photoconductivity of critical dye pairs of known (?) polarographic potentials. The action of a spectroscopically degenerate but polarographically different set of dyes was shown not to be explicable in terms of the simple theory of supersensitization by hole-trapping which is currently being emphasized. Critical examination of the polarographic data on dyes indicates that much of this data is unreliable for classifying dyes.

The induction of circular dichroism in the absorption bands of cationic dyes in a chiral, anionic medium (sodium desoxycholate micelles) was shown to be a simple, nonphotographic test for distinguishing twisted, antisensitizing dyes from sensitizers.

Clarification of the problem of incomplete light absorption by sensitizing dyes through surface studies and the formulation of a conservation theorem for light absorption by dyes on surfaces. This work also led to the concept of systems giving high sensitivity over a narrow spectral band for laser applications.

Theoretical analysis of the ultimate capabilities (detective quantum efficiency) of organic imaging systems. This analysis led to the discovery of a new class of systems, the Noiseless Chemical Amplifiers.

Recognition of the critical importance of thermal pseudoimage forming reactions in high sensitivity organic systems and the development of general strategies for combatting these thermal reactions.

Measurement of the primary quantum yield in the system of leuco crystal violet and CBr_4 and separation of the multiple reaction products. This work corrected an erroneous and discouragingly low quantum yield in the literature.

Observations on the morphology and electron diffraction patterns of single microcrystals in silver halide-gelatin emulsions.

Analysis of the gains in photographic sensitivity and in detective quantum efficiency to be obtained from production of negative materials optimized for latensification.

AFOSR Program Manager: Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: Stabilized Detonation on Wave Chemical Laser Systems
2. PRINCIPAL INVESTIGATOR: Dr. J. R. Bowen
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Madison, Wisconsin 53706
3. INCLUSIVE DATES: 1 February 1971 to 30 June 1975
4. GRANT NUMBER: AFOSR-71-2033
5. COSTS AND FY SOURCE: \$29,977 FY 71; \$20,000 FY 73
\$23,200 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. A. Akyurtlu
Dr. R. W. Dibble
Dr. C. T. Moses
Dr. M. J. R. Schwar
7. JUNIOR RESEARCH PERSONNEL: Ward Hanson
Barbara Morin

8. PUBLICATIONS:

"An Experimental and Theoretical Investigation of Photolytic and Gas Dynamic Laser Systems," C. T. Moses, Ph.D. Dissertation, University of Wisconsin-Madison, May 1972.

"Measurements of the Local Velocity of Shock and Detonation Waves by Schlieren Interferometry of Doppler-shifted Laser Light," M. J. R. Schwar, and J. R. Bowen, J. Phys. D: Appl. Phys. 5, 1561-1575 (1972).

"An Investigation of the Structure and Detonability Limits of Hydrogen-Chlorine Detonations," Ates Akyurtlu, Ph.D. Dissertation, University of Wisconsin-Madison, July 1975.

"Laser Probing of Excited CO Products from Shock Wave Initiated Oxidation of Carbon Disulfide," R. W. Dibble, Ph.D. Dissertation, University of Wisconsin-Madison, October 1975.

"Studies of a Chemical Reaction in a Shock Tube by Tuned Laser Spectroscopy," R. W. Dibble and J. R. Bowen, in preparation.

"Estimation of Pressure Limits of Detonability in H_2-Cl_2 -Ar Mixtures," Ates Akyurtlu and J. R. Bowen, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research has been concerned with the development of a new fluid mechanical chemical laser system, and with the application of a laser as a diagnostic tool to obtain experimental data on population distributions and more precise localized velocity data for shock and detonation waves.

Stabilized Detonation Wave Laser (SDW)

An improved experimental system for the SDW laser concept has been designed and fabricated. Prior to testing the system an extensive investigation of detonability limits was undertaken to provide basic data needed to select operating conditions.

Pressure limits of detonations in hydrogen-chlorine and hydrogen-chlorine-40% argon mixtures were established experimentally. It was found that at 300°K no mixture of hydrogen, chlorine and argon could be detonated below 16 torr. Replacement of excess hydrogen with argon considerably lowered the pressure limits. Replacing some of the chlorine with argon had the reverse effect. This behavior was attributed to the decrease in the induction time in chlorine rich mixtures and to the higher specific heat of hydrogen molecule.

A method was proposed for the prediction of pressure limits, if a limit for one mixture composition and the variation of the characteristic blast wave radius for the detonation with system pressure and composition is known.

The detonation velocities measured were all significantly above the theoretical Chapman-Jouget velocities. It is believed that although most of the detonations were overdriven, a significant portion of the differences between experimental and theoretical velocities is due to only a partial thermodynamic equilibrium at the detonation end state.

Detonations in hydrogen-chlorine and hydrogen-chlorine-argon mixtures exhibited an irregular tridimensional structure on the soot records. Although an equilibrium configuration could not be obtained, the measurements performed on the soot records gave satisfactory results. The cell size decreased with pressure. Ratio of cell length to sonic speed creased with pressure. Ratio of cell length to sonic speed in the unburned gas showed a power dependence on pressure. The incidence angles had an average value of 72° and showed no dependence on mixture composition and initial pressure.

Laser Doppler Velocimetry

A new method of measuring the local velocity of shock and detonation waves, based on measuring the Doppler shift in frequency of laser light using Schlieren interferometry, is reported and its limitations are assessed. Expressions are given for the Doppler shift in terms of all the relevant parameters, including the refraction produced at the windows of the detonation vessel, for the spatial resolution, and for the accuracy of the method. Velocity measurements made on stoichiometric oxygen-acetylene mixtures at an initial pressure of 75 torr show that, prior to the onset of detonation, local shock wave velocity measurements can be made over a distance of 4.4×10^{-3} cm with an accuracy of $\pm 11\%$, and 4.4×10^{-2} cm with an accuracy of $\pm 2\%$. For the detonation wave the error in the velocity measurement was about $\pm 20\%$ when averaged over distances of 1 to 2×10^{-1} cm.

Tuned Laser Spectroscopy

Macroscopic kinetic parameters such as induction times and/or laser gain coefficients may be determined by probing certain gaseous systems with a laser tuned to match the accessible vibrational-rotational states of a reaction product. In principle, nascent and transient population distributions may also be calculated for such systems from the amplification or attenuation of the probe beam.

In this study, the transient populations of vibrationally excited carbon monoxide formed by the oxidation of carbon disulfide in a shock tube was monitored by a tuned cw carbon monoxide laser. Excited carbon monoxide was produced by the reaction $\text{CS} + \text{O} \rightarrow \text{CO}^+ + \text{S}$. A frequency stabilized 1.8 meter electric discharge laser, cooled in a dry ice-methanol bath, was tunable over the vibrational transitions $v = 15-14$ to $v = 7-6$ with rotational levels $J = 15 \pm 2$. Typical conditions behind the reflected shock in a 95% oxygen - 5% carbon disulfide mixture were $p = 550$ torr, $T = 900^\circ\text{K}$.

In a typical experiment the following features were noted. After an induction time of approximately 600 μsec , amplification of the laser beam was observed and lasted for about 70 μsec . Beam attenuation immediately followed amplification and lasted about 130 μsec . These general features were reproducible, although the quantitative gain/loss data showed some scatter. The greatest gain/loss ($\sim 0.5\% \text{ cm}^{-1}/1\% \text{ cm}^{-1}$) was observed on the $v = 10-9$ transition; this result is consistent with results obtained from CS_2 - O_2 flame laser experiments.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Spectroscopic Studies of Energy Exchange Processes
2. PRINCIPAL INVESTIGATOR: Dr. H. P. Broida
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3. INCLUSIVE DATES: 1 September 1969 to 31 August 1974
4. GRANT NUMBER: AFOSR-70-1851
5. COSTS AND FY SOURCE: \$42,161 FY 71; \$44,633 FY 72
\$45,632 FY 73; \$48,217 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. R. S. Bradford
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Dr. John Clark
Dr. C. J. Duthler
Dr. J. D. Eversole
Dr. R. W. Field
Dr. J. M. Flournoy
Dr. S. E. Johnson
Dr. C. R. Jones
Dr. C. Liu
Dr. M. S. Manalis
Dr. D. M. Mann
Dr. E. Miescher
Dr. L. Y. Nelson
Dr. Leonard Nelson
Dr. R. J. Oldman
Dr. K. Sakurai
Dr. R. D. Verma
Dr. J. B. West
7. PUBLICATIONS:
"Rotational Excitation During Ion-Molecule Collisions," C. Liu,
J. Chem. Phys. 53, 1295 (1970).
"Fluorescence of Na₂ Induced by a Helium-Neon Laser at 632.8 and
640.1 nm," S. E. Johnson, K. Sakurai and H. P. Broida, J. Chem.
Phys. 52, 6441 (1970).
"Laser Induced Fluorescence of BaO," S. E. Johnson, K. Sakurai and
H. P. Broida, J. Chem. Phys. 52, 1625 (1970).
"SO₂ Infrared Fluorescence," L. Y. Nelson and H. P. Broida, J. Chem.
Phys. 53, 1283 (1970).
"Vibrational Excitation of HCN," J. M. Flournoy and L. Y. Nelson,
Chem. Phys. Letrs. 6, 521 (1970).
"Spectral Study of the Phosphorus Glow," R. D. Verma and H. P.
Broida, Can. J. Phys. 48, 2992 (1970).

"Optical Spectra Observed During Ion-Molecule Collisions Using Low-Energy N_2^+ and Ar^+ Beams," C. Liu and H. P. Broida, Phys. Rev. 2, 1824 (1970).

"Laser Induced Fluorescence of ClO_2 ," K. Sakurai, J. Clark and H. P. Broida, J. Chem. Phys. 54, 1217 (1971).

"Fluorescence Lifetime Measurement of the \tilde{A} State of Formaldehyde Excited by a 3371 Å Nitrogen Pulsed Laser," K. Sakurai, C. Capelle, and H. P. Broida, J. Chem. Phys. 54, 1412 (1971).

"Lifetimes and Self-Quenching Cross Sections of Vibrational Levels in the B State of Bromine Excited by a Tunable Dye Laser," G. Capelle, K. Sakurai, and H. P. Broida, J. Chem. Phys. 54, 1728 (1971).

"Ultraviolet Absorption Spectra of Transition Metal Atoms in Rare-Gas Matrices," D. M. Mann and H. P. Broida, J. Chem. Phys. 55, 84 (1971).

"Vibrational Distributions of the N_2 First Positive System Produced in a Flowing Helium Afterglow," M. S. Manalis and H. P. Broida, Mol. Phys. 20, 947 (1971).

"Spectroscopy of Selected Diatomic Metal and Metal-Oxide Molecules Using Laser Excited Fluorescence," S. E. Johnson, Ph.D. Thesis, Univ. of Calif., Santa Barbara, Ca. (1971).

"Excitation of Neutral Atomic Nitrogen in a Helium Afterglow," M. S. Manalis and H. P. Broida, Spectrochimica Acta 26B, 721 (1971).

"Measured Radiative Lifetimes and Electronic Quenching Cross Sections of BaO ($A^1\Sigma$)," S. E. Johnson, J. Chem. Phys. 56, 149 (1972).

"Laser Excited Fluorescence and Radiative Lifetimes of AlO ($B^2\Sigma^+ - X^2\Sigma^+$)," S. E. Johnson, G. A. Capelle, and H. P. Broida, J. Chem. Phys. 56, 663 (1972).

"Microwave Optical Double Resonance Spectroscopy of BaO ," R. W. Field, R. S. Bradford, D. O. Harris, and H. P. Broida, J. Chem. Phys. 56, 4712 (1972).

"New Molecular Constants for the Ground Electronic State of Pb_2 ," S. E. Johnson, D. Cannell, J. Lunacek and H. P. Broida, J. Chem. Phys. 56, 5723 (1972).

"Excited State Microwave Spectroscopy on the $A^1\Sigma$ State of BaO ," R. W. Field, R. S. Bradford, H. P. Broida and D. O. Harris, J. Chem. Phys. 57, 2209 (1972).

"Microwave Optical Double Resonance Spectroscopy with a CW Dye Laser: BaO $X^1\Sigma$ and $A^1\Sigma$," R. W. Field, A. D. English, T. Tanaka, D. O. Harris and D. A. Jennings, J. Chem. Phys. 59, 2191 (1973).

"Microwave Optical Double Resonance of NO_2 with a Tunable CW Dye Laser," T. Tanaka, A. D. English, R. W. Field, D. A. Jennings and D. O. Harris, J. Chem. Phys. 59, 5217 (1973).

"Chemiluminescence Reactions Involving Metal Vapors," C. J. Duthler and H. P. Broida, Chemiluminescence and Bioluminescence, Plenum, p. 101, (1973).

"Excitation of Group Ia and IIb Metal Atoms by a Lewis-Rayleigh Nitrogen Afterglow," C. J. Duthler and H. P. Broida, J. Chem. Phys. 59, 167 (1973).

"Chemiluminescence and Photoluminescence of some Diatomic Metal Halides," G. A. Capelle, R. S. Bradford and H. P. Broida, Chem. Phys. Letrs. 21, 418 (1973).

"Direct Observation of Vibrationally Excited Hydrogen Produced by Collisional Energy Transfer from Electronically Excited Sodium, Rubidium, Caesium and Mercury," P. H. Lee, W. Braun, J. T. Herron, and H. P. Broida, J. Photochem. 2, 165 (1973).

"Near-Infrared ${}^2\Delta - {}^2\Pi$ Nitric Oxide Laser with Predissociated Lower State," H. P. Broida and E. Miescher, IEEE J. Quant. Elec. 9, 1029 (1973).

"An Efficient Chemiluminescent Reaction," C. R. Jones and H. P. Broida, J. Chem. Phys. 59, 6677 (1973).

"How Basic Research Might Contribute to the Alleviation of Air Pollution," H. P. Broida, Environmental Problems and Their International Implications, Colorado Assoc. Univ. Press, p. 1 (1973).

"Electronic-Transition Chemical Lasers," C. R. Jones and H. P. Broida, Laser Focus 10, No. 3, 37 (1974).

"Gas-Phase Reaction of Ba with N_2O . I. Measurement of Production Efficiency of Excited States," C. R. Jones and H. P. Broida, J. Chem. Phys. 60, 4369 (1974).

"Gas-Phase Reaction of Ba with N_2O . II. Mechanism of Reaction," R. W. Field, C. R. Jones and H. P. Broida, J. Chem. Phys. 60, 4377 (1974).

"Microwave Optical Double Resonance Spectroscopy of Metal Oxides," D. O. Harris, R. W. Field and H. P. Broida, Ber. Bunsenges. Physik. Chemie 78, 146 (1974).

"Laser Photoluminescence and Photopredissociation of Rb_2 ," J. M. Brom, Jr. and H. P. Broida, J. Chem. Phys. 61, 982 (1974).

"Photon Yields and Spectra Resulting from Reactions of Ca with Oxidants," G. A. Capelle, C. R. Jones, J. Zorskie, J. Chem. Phys. 61 xxxx (1974).

"Flow System for The Production of Diatomic Metal Oxides and Halides," J. B. West, R. S. Bradford, Jr., J. D. Eversole and C. R. Jones, Rev. Sci. Instrum. (accepted)

"Production Efficiencies of Electronically Excited States of Barium Monohalides," R. S. Bradford, Jr., C. R. Jones, L. A. Southall and H. P. Broida, J. Chem. Phys. (submitted).

"Chemiluminescence and Photoluminescence Spectroscopy of the Barium Monohalides," R. S. Bradford, Ph.D. Thesis, Univ. of Calif. Santa Barbara, Ca. (1974).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The Objective of this program has been to study gas phase kinetics through the use of unique optical spectroscopy techniques developed at the University of California, Santa Barbara. Research has been focused on processes involving electronic and vibrationally excited states. Optical spectroscopy from 100 to 20,000 nm has been used to determine mechanisms and to measure rate constants and cross sections for several low energy collision processes and chemiluminescent reactions involving small molecules. Studies have included: (A) development of new, ultrahigh resolution optical methods for the study of molecules; (B) use of improved laser facilities to measure more accurately the kinetics of room temperature metal atoms reactions with oxidants and halogens; and (C) use of laser induced photoluminescence to measure spectroscopic constants of other simple molecular species which are of atmospheric, combustion, and chemical laser interest.

Most of these recent efforts have been directed towards optical spectroscopic study of gas-phase diatomic metal, metal-oxide and metal-halide molecules. Several vacuum flow systems have been developed for molecular production. A metal sample is placed in a ceramic crucible surrounded by a tungsten wire basket which is resistively heated. Resulting metal vapor is entrained in a flow of inert carrier gas and is transported into the reaction region where an oxidizing gas is injected. Reactions usually result in bright chemiluminescent flames. From emission spectra, various molecular constants and kinetic information are obtained. Ground electronic states have been probed with laser-induced photoluminescence.

Chemiluminescence studies have included BaO, CaO, CaF, CaCl, CaBr, BaX (X=F, Cl, Br, I) and BiCl, BiBr, CuCl, CuBr, PbCl, PbBr. Using spectra obtained from chemiluminescence, photon yields (number of photons emitted per reacted metal atom) have been obtained for Ba + N₂O; CaO, CaF, CaBr, CaCl; and BaX.

The photon yield for BaO (A-X) is strongly dependent on inert-gas pressure and has been measured to be 0.22 photons per reacted Ba atom at pressures near 10 torr. Also at this pressure, the specific yield for production of BaO A-state molecules in a single vibrational level, v=1, is found to have the surprising large value of 0.08. A reaction mechanism has been proposed in which most BaO molecules are formed initially in the long-lived a ³Π state and are transferred subsequently by collisions into the shorter-lived A ¹Σ⁺ state. This mechanism accounts for numerous kinetic and spectroscopic observations of BaO.

Laser-induced photoluminescence (fluorescence) has been a powerful tool in the study of Na₂, BaO, ClO₂, Pb₂, BaX, BiCl, BiBr, CuCl, CuBr, PbCl, PbBr, and Rb₂.

BaO photoluminescence was induced by two lines of an Ar⁺ laser. The strongest A ¹Σ - X ¹Σ emission was observed from v'=8, J'=49 excited by 488.0 nm and v'=7, j'=3 and 7 excited by 496.5 nm.

Studies were made, from 0.4 to 40 torr, of collisional energy transfer to other rotational and vibrational levels of the A state after optical pumping by the laser.

A single mode Ar^+ laser at 514.5 nm was used to induce photoluminescence in Pb_2 . The resulting spectra lead to new ground state constants: $\omega_e=109.1\pm0.3$ and $\omega_e x_e=0.35\pm0.04 \text{ cm}^{-1}$. Vibrational number of many bands were reassigned.

Fixed frequency ion lasers and a tunable cw dye laser were used to excite photoluminescence in Rb_2 at pressures from 1 to 100 torr of metal vapor contained in a heat pipe oven. Studies show that the $\text{C } ^1\Pi_u$ state is strongly predissociated and that $\text{A } ^1\Sigma_u$ and $\text{B } ^1\Pi_u$ states are also populated following absorption by the $\text{C } ^1\Pi_u$ state. Recombination collisions between $\text{Rb } 5^2\text{P}$, formed in the predissociation of Rb_2 , and $\text{Rb } 5^2\text{S}$ have been proposed to account for A-X and B-X emission.

A complete rotational assignment has been made of four NO_2 absorption lines at 593.6 nm by MODR using a cw dye laser. Various fine and hyperfine components of $9_{1,9} \rightarrow 10_{0,10}$ rotational transition of the ground vibronic state of NO_2 are near 40 GHz. Microwave frequencies used in the experiment were 40.671, 40.703 and 40.931, 40.964, 40.933 which correspond to $J=19/2 \rightarrow 21/2$ and $J=17/2 \rightarrow 19/2$, respectively. Observed optical transitions near 593.6 nm were assigned to $10_{0,10}(21/2) \rightarrow 9(19/2)$, $10_{0,10}(19/2) \rightarrow 9(17/2)$, $9_{1,9}(19/2) \rightarrow 8(17/2)$ and $9_{1,9}(17/2) \rightarrow 8(15/2)$.

Radiative lifetimes of electronic states of several molecules have been measured from the photoluminescence decay excited by a short-pulsed (10 nsec) tunable dye laser.

This has been used to excited selected vibrational levels between $v'=1$ and 31 of the $\text{B } ^3\Pi_{Ou}$ state of Br_2 . Lifetimes and self-quenching cross sections were measured by observing the direct decay of fluorescence as a function of pressure. Large variations of lifetimes and cross sections were found; lifetimes varied by a factor of 8, ranging from greater than 1.2 msec near $v'=27$ to less than 0.15 msec near $v'=14$. Two minima of lifetimes near $v'=1$ and 14 are due to decay of the B state by spontaneous predissociation through dissociative states.

Lifetimes of the $\text{A } ^1\Sigma$ state of BaO were measured for $v'=0$ to 11 and were found to vary from 275 ± 22 to 389 ± 16 nsec. Quenching cross sections of $\text{BaO } (\text{A } ^1\Sigma)$ by He varied with vibrational level over the range 0.3 to $2.3 \times 10^{-16} \text{ cm}^2$.

Flowing afterglow experiments were performed with both He and N_2 as the active species. In the former, the afterglow is initiated by a dc discharge while the latter by a 2450 MHz microwave discharge.

A light source of neutral N atoms was developed by mixing traces of N_2 in a flowing He afterglow at pressures near 1 torr. This source produces radiation from energy levels near the ionization limit of the neutral atom but none from excited states of N^+ . Excited N atoms are produced by recombination of electrons with N^+ formed in dissociative charge transfer reactions of He^+ with N_2 . Approximately 400 new N atom lines were found. A second mechanism

was found in which N_2 is dissociated by metastable molecular helium then excited by collisions with energetic electrons. The characteristic temperature associated with this level population distribution was about $10^4 K$.

Hydrogen was vibrationally excited by direct energy transfer from electronically excited Na, Rb, Cs and Hg. Vibrational excitation of $B^1\Sigma_u + X^1\Sigma_g^+$ transitions in H_2 was detected by absorption of vacuum uv radiation from a low pressure H_2 lamp.

Vibrational excitation of HCN was obtained by mixing in a stream of vibrationally excited N_2 , H_2 or D_2 produced by a microwave discharge. More than 60 lines were resolved near $3\mu m$ and consisting primarily of the ν_3 fundamental C-H stretch.

Infrared emission has been observed from SO_2 at 7.4 and $8.7 \mu m$ when ground state SO_2 molecules collided with a flowing stream of active nitrogen produced by a 2440 MHz microwave discharge. The $7.4 \mu m$ emission was assigned to $(001) \rightarrow (000)$ while $8.4 \mu m$ is due to $(100) \rightarrow (000)$.

A bright flame produced by the reaction of O atoms with white phosphorous has been developed. In addition to a visible continuum, emission consists of several PO transitions and the $A^1\Pi_g - X^1\Sigma_g^+$ transitions of P_2 . Atomic oxygen and a third body such as H_2O or H_2 is found essential for the production of discrete bands. Pressure effects on the intensity of PO β -bands indicate the presence of a heterogeneous perturbation in the $B^2\Sigma(v=7)$ level by a $2\Pi_r$ state.

A pulsed NO laser at $1.02 \mu m$ has been produced. The spectrum was photographed with high resolution and rotational analysis fully confirms assignment of the transition to $F^2\Delta - C^2\Pi(1,1)$. Both of these electronic states are configurationally mixed with valence levels.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Prediction of Properties and Behavior of Materials
2. PRINCIPAL INVESTIGATOR: Dr. Michael J. S. Dewar
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3. INCLUSIVE DATES: 1 September 1971 to 31 August 1974
4. CONTRACT NUMBER: F44620-71-C-0119
5. COSTS AND FY SOURCE: \$149,358 FY 72; \$152,903 FY 73
\$108,081 FY 74; \$26,919 FY 75
6. SENIOR RESEARCH PERSONNEL: Dr. Richard C. Bingham
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Dr. Robert C. Haddon
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Edmond J. Mantooth
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Ignatius J. Turchi
Leslie E. Wade
Paul K. Weiner
8. PUBLICATIONS:

"The Barrier to Pyramidal Inversion of Nitrogen in Dibenzylmethylaniline,"
M. J. S. Dewar and W. B. Jennings, J.A.C.S. 93, 401 (1971).

"Nuclear Quadrupole Resonance Spectra of Some Alkylaluminum Derivatives,"
M. J. S. Dewar, Dennis B. Patterson, and W. Irven Simpson, J.A.C.S. 93, 1030
(1971).

"Cope Rearrangements in the Bullvalene Series," M. J. S. Dewar and Wolfgang W.
Schoeller, J.A.C.S. 93, 1481 (1971).

"MINDO/2 Calculations of Nuclear Quadrupole Coupling Constants of the Chloro-
benzenes," M. J. S. Dewar, D. H. Lo, D. B. Patterson, N. Trinajstić, and
G. E. Peterson, J. Chem. Soc., Chem. Commun., 239 (1971).

- "Trimethylenemethane and the Methylenecyclopropane Rearrangement", M. J. S. Dewar and J. S. Wasson, J.A.C.S., 93, 3081 (1971).
- "New Heteroaromatic Compounds. XXXIII. 5,1,3,4-Boratriazaroles", M. J. S. Dewar, R. Golden, and P. A. Spanninger, J.A.C.S., 93, 3298 (1971).
- "MINDO/2 Study of Aromatic ("Allowed"), Electrocyclic Reactions of Cyclopropyl and Cyclobutene", M. J. S. Dewar and S. Kirschner, J.A.C.S., 93, 4290 (1971).
- "MINDO/2 Study of Antiaromatic ("Forbidden") Electrocyclic Processes", M.J.S. Dewar and S. Kirschner, J.A.C.S., 93, 4291 (1971).
- "Classical and Nonclassical Potential Surfaces. The Significance of Anti-aromaticity in Transition States", M.J.S.Dewar and S. Kirschner, J.A.C.S., 93, 4292 (1971).
- "Protonation of Cyclopropane", N. Bodor and M. J. S. Dewar, J.A.C.S., 93, 6685 (1971).
- "Ground States of σ -Bonded Molecules. XIII. 7-Norbornyl, 7-Norbornenyl and 7-Norbornadienyl Ions and Radicals", M. J. S. Dewar and W. W. Schoeller, Tetrahedron, 27, 4401 (1971).
- "Aromaticity and Pericyclic Reactions", M. J. S. Dewar, Angew. Chemie, Int. Ed., 10, 761 (1971).
- "Additivity of Bond Energies in the Light of the Maximum Overlap Approximation (MOA) and MINDO/3", M.J.S.Dewar, D.H.Lo, and Z.B.Maksic, Croat. Chem. Acta, 46, 7 (1974).
- "Diazabullvalene; a "Nonclassical" Molecule?" M.J.S.Dewar, Z. Nahlovsky and B.D.Nahlovsky, J. Chem. Soc., Chem. Commun., 1377 (1971).
- "Ground States of σ -Bonded Molecules. XIV. Application of Energy Partitioning to the MINDO/2 Method and a Study of the Cope Rearrangement", M.J.S.Dewar and D.H.Lo, J.A.C.S., 93, 7201 (1971).
- "Abundant Rearrangement Ions in the Mass Spectra of Benzeneboronic Acid Derivatives", C. Cone, M.J.S.Dewar, R. Golden, F. Maseles, and P. Rona, J. Chem. Soc., Chem. Comm., 1522 (1971).
- "MO Theory as a Practical Tool for Studying Chemical Reactivity", M.J.S.Dewar, Topics in Current Chemistry, Fortschr. Chem. Forsch., 23, 1 (1971).
- "New Heteroaromatic Compounds. XXXIV. Bisboratriazaroles", M.J.S.Dewar and P. A. Spanninger, Tetrahedron, 28, 959 (1972).
- "Ground States of σ -Bonded Molecules. XV. Barriers to Rotation About Carbon-Carbon Bonds", M. J. S. Dewar and M. C. Kohn, J.A.C.S., 94, 2699 (1972).
- "Ground States of σ -Bonded Molecules. XVI. The Rearrangement of Methyl Isocyanide to Acetonitrile", M. J. S. Dewar and M. C. Kohn, J.A.C.S., 94, 2704 (1972).
- "Ground States of σ -Bonded Molecules. XVII. Fluorine Compounds", M. J. S. Dewar and D. H. Lo, J.A.C.S., 94, 5296 (1972).
- "Ground States of σ -Bonded Molecules. XVIII. An improved Version of MINDO/2 and Its Application to Carbonium Ions and Protonated Cyclopropanes", N.Bodor, M.J.S. Dewar and D. H. Lo, J.A.C.S., 94, 5303 (1972).

- "Mechanism of Rearrangement of Alkyl Phenyl Ethers Catalysed by Aluminum Bromide", M.J.S.Dewar and P. A. Spanninger, J.Chem. Soc., Perkin Trans. II, 1204 (1972).
- "Ground States of Molecules. XXI. MINDO/2 Potential Surfaces for Ethane", M.J.S.Dewar and H. Metiu, Proc. Roy. Soc. London A, 330, 173 (1972).
- "Photoelectron Spectra of Molecules. V. Polycyclic Aromatic Hydrocarbons", M.J.S.Dewar and D. W. Goodman, J. Chem. Soc., Faraday Trans. II, 68, 1784 (1972).
- "Ground State of Molecules. XIX. Carbene and Its Reactions", N. Bodor, M.J.S. Dewar and J. S. Wasson, J.A.C.S., 94, 9095 (1972).
- "Ground States of Molecules. XX. MINDO/2 Study of Some Carbenes and Their Intramolecular Rearrangements", N. Bodor and M.J.S.Dewar, J.A.C.S., 94, 9103 (1972).
- "Ground States of Molecules. XXII. Incorporation of Partial Configuration Interaction in MINDO/2 and Its Application to Bond Dissociation Energies and Sigmatropic Rearrangements", R. C. Bingham and M. J. S. Dewar, J.A.C.S. 94, 9107 (1972).
- "Ground States of Molecules. XXIII. MINDO/2 Calculations for Naphthalene", M.J.S.Dewar and P. Weiner, Theoret. Chim. Acta (Berl.), 27, 373 (1972).
- "The Possible Role of 1,4-Cyclohexylene Intermediates in Cope Rearrangements", M.J.S.Dewar and L.E.Wade, J.A.C.S., 95, 290 (1973).
- "Conformational Interchange in Acyclic Hydrazines", M.J.S.Dewar and W. B. Jennings, J.A.C.S., 95, 1562 (1973).
- "MINDO/3 Study of $(CH)_5^+$ and $(CH)_5^-$ ", M.J.S.Dewar and W. B. Jennings, J.A.C.S. 95, 5836 (1973).
- "Ground States of Molecules. XXIV. MINDO/2 Study of Some Reactions of Cyclopropylidene", N.Bodor, M.J.S.Dewar, and Z.B.Maksic, J.A.C.S., 95, 5245 (1973).
- "The Photoelectron Spectrum of Phosphorus Pentafluoride", D. W. Goodman, M.J.S. Dewar, J.R.Schweiger, and A. H. Cowley, Chem. Phys.Let, 21, 3 (1973).
- "Stereochemical Dependence of Lone Pair Interactions in the Photoelectron Spectra of Nitrogen-Phosphorus Compounds", A.H.Cowley, M.J.S.Dewar, D.W.Goodman, and J.R. Schweiger, J.A.C.S., 95, 6506 (1973).
- "A MINDO/3 Study of the Factors Controlling Configurational Stability in Vinyl and Cyclopropyl Radicals", R.C.Bingham, M.J.S.Dewar, J.A.C.S., 95, 7180 (1973).
- "Antagonism Between Substituents in Radicals", R. C. Bingham, M.J.S.Dewar, J.A.C.S. 95, 7182 (1973).
- "A MINDO/3 and NDDO Study of Antiaromatic Three-Membered Rings and Their Valence Tautomers", M.J.S.Dewar and C.A. Ramsden, J.Chem. Soc., Chem. Commun., 978 (1973).
- "Substituent Effects. XI. Polar and π -Electron Substituent Effects by ^{19}F Nuclear Magnetic Resonance", W.Adcock, M.J.S.Dewar, and B.D.Gupta, J.A.C.S., 95, 7353 (1973).
- "A Study of Bonding in Some Organoaluminum Compounds by ^{27}Al Nuclear Quadrupole Resonance Spectroscopy", M.J.S.Dewar, D.B.Patterson, and W.I.Simpson, J.Chem.Soc. Dalton Trans. 2381 (1973).

- "Nature of the Intermediate in the Cornforth Rearrangement", M.J.S.Dewar, P.A. Spanninger, and I.J.Turchi, J.Chem. Soc., Chem. Commun., 925, (1973).
- "MINDO/3 Study of the Electronic States of Methylene", M.J.S.Dewar, R.C. Haddon, P.K.Weiner, J.A.C.S., 96, 253 (1974).
- "MINDO/3 Study of the Multiplicity of Cyclopentadienate Cations", M.J.S.Dewar, R.C.Haddon, J.A.C.S., 96, 255 (1974).
- "Claisen Rearrangement of Cinnamyl Phenyl Ether in Isotropic and Nematic Solvents and in a Clathrate", M.J.S.Dewar and B.D.Nahlovsky, J.A.C.S., 96, 460 (1974).
- "Detection of Rotational Isomerism in Diphosphines and Diarsines by Photoelectron Spectroscopy", A.H.Cowley, M.J.S.Dewar, D.W.Goodman, M.C.Padolina, J.A.C.S., 96, 2648 (1974).
- "A Photoelectron Spectroscopic Study of Polyphosphines. The Question of $p\pi:d\pi$ Bonding", A.H.Cowley, M.J.S.Dewar, D.W.Goodman, M.C. Padolina, J.A.C.S., 96, 3666 (1974).
- "Relationship Between the Photoelectron Spectra and Torsional Barriers of Aminophosphines", A.H.Cowley, M.J.S.Dewar, J.W.Gilje, D.W. Goodman, and J.R. Schweiger, J. Chem. Soc., Chem. Commun., 340 (1974).
- "Orbital Isomerism as a Controlling Factor in Chemical Reactivity", M.J.S.Dewar, S.Kirschner, H.W.Kollmar, J.A.C.S., 96, 5240 (1974).
- "Orbital Isomerism in Biradical Processes", M.J.S.Dewar, S.Kirschner, H.W. Kollmar, L.E.Wade, J.A.C.S., 96, 5242 (1974).
- "Nature of the Transition States in "Forbidden" Electrocyclic Reactions", M.J.S. Dewar, S.Kirschner, J.A.C.S., 96, 5244 (1974).
- "Dimerization of Ethylene to Cyclobutane", M.J.S.Dewar, S.Kirschner, J.A.C.S., 96, 5246 (1974).
- "MINDO/3 Study of [18] Annulene", M.J.S.Dewar, R.C.Haddon, and P.J.Student, J.Chem Soc. Chem. Commun., 569 (1974).
- "MINDO/3 Study of Bisdehydrobenzenes", M. J. S. Dewar, W. K. Li, J.A.C.S., 96, 5569 (1974).
- "The Cornforth Rearrangement", M. J.S.Dewar and I. J. Turchi, J.A.C.S., 96, 6148 (1974).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The most important achievement resulting from the research has been the development of a quantum mechanical treatment that for the first time enables the detailed course of chemical reactions to be studied with reasonable accuracy and reliability and at reasonable cost. Applications of MINDO/II and MINDO/III to a very wide variety of chemical problems have led to a new insight into the mechanisms of many organic reactions and to conclusions which are not only important but often totally unexpected.

A second area has been concerned with molecular (uv) photoelectron spectroscopy. A 127° sector type spectrometer was constructed following the general design to Turner which seems to be at least five times more sensitive than any previously described. The spectrometer has been used to study a number of problems concerning bonding in compounds of Group IV and Group V elements.

Another project has been concerned with nuclear quadrupole resonance (nqr) spectroscopy. Here again an instrument was built since the only commercial one currently available was not at all satisfactory. It has been used mainly to study bonding in organometallic compounds, in particular of aluminum and cobalt, although a good deal of work has also been done on chlorine nqr spectra.

In the nmr field, the concern was with the magnitude and nature of the barriers to rotation about bonds between Group V elements (NN, NP, NAs) and with the barriers to inversion in pyramidal nitrogen.

Another area studied is that of liquid crystals. Here the concern was with the relationship between structures and mesophase stability, with attempts to prepare new types of nematic liquid crystals, in particular compounds of greater stability than those currently used and new types of cholesteric materials, and with attempts to obtain liquid crystalline glasses. A large number of new liquid crystals were prepared during the course of this work and measurements of their heats of transition to normal liquids led to some novel and unexpected conclusions concerning the relationship between structure and mesophase stability.

The mechanisms of several molecular rearrangements have been studied experimentally partly because of their inherent interest and partly because the information was needed to interact with the theoretical studies. These included the Cope rearrangements of a number of derivatives of 1,5-hexadiene containing aryl and vinyl substituents and a number of Cornforth rearrangements of oxazole derivatives.

In the area of organoboron chemistry, a new stable boron containing five-membered heterocycle was discovered; polymers derived from it seem to show interesting stability at high temperatures.

Previous work had shown that the effects of substituents on F^{19} chemical shifts are not at all closely related to their effects on chemical reactivity; additional information concerning this was obtained by studies of a number of fluorine compounds specifically synthesized for the purpose.

A number of other projects are still incomplete. These include the preparation of new metal coordination polymers as potential semiconductors, the construction of a photoelectron spectrometer with a molecular beam source, and studies of the reactions of energetic species produced in microwave plasmas.

The research done under this contract is described in detail in the papers published or submitted for publication.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Reactivity Patterns Characteristic of Lighter Metallic Elements (Titanium)
2. PRINCIPAL INVESTIGATOR: Dr. Joseph E. Earley
Department of Chemistry
Georgetown University
Washington, DC 20007
3. INCLUSIVE DATES: 1 May 1971 to 31 December 1974
4. GRANT NUMBER: AFOSR-71-2003
5. COSTS AND FY SOURCE: \$13,269 FY 71; \$38,823 FY 73
\$24,567 FY 74
6. SENIOR RESEARCH PERSONNEL: Keith M. Davies
Mato Orhanovic
7. JUNIOR RESEARCH PERSONNEL: S. Z. Ali T. Fealey
L. P. Bignetti R. Grillo
P. Chalilpoyil C. Rowe
F. A. Czulada J. G. Zimmerman
8. PUBLICATIONS:

"The Crystal and Molecular Structure of Di- μ -oxo-bis(pentaammineruthenium) bis(ethylenediamine)ruthenium Hexachloride. The Ethylenediamine Analog of 'Ruthenium Red'," Peter M. Smith, Terence Fealey, Joseph E. Earley and J. V. Silverton, Inorg. Chem. **10**, 1943 (1971).

"A Triplet Ground State for a Dimeric Cation with a Metal-Metal Bond: $[(\text{NH}_3)_4\text{Ru}(\text{NH}_2)_2\text{Ru}(\text{NH}_3)_4]^{4+}$," Joseph E. Earley, Terence Fealey, M. T. Flood, Harry B. Gray, Albert Schweizer and J. Thibeault, Proc. of the Internat. Conf. on Coord. Chem. **14**, 361 (1972).

"Hydroxide Ion as a Reducing Agent for Cations Containing Three Ruthenium Atoms in Nonintegral Oxidation States," Joseph E. Earley and Terence Fealey, Inorg. Chem. **12**, 323 (1973).

"Trans-Labilization of Water by Thiourea and by Thiosulfate Ion as Ligands in Bis-(Dimethylglyoximate)-Cobalt(III) Complexes," Joseph E. Earley and John G. Zimmerman, Inorg. and Nucl. Chem. Ltrs. **8**, 687 (1972).

"The Crystal and Molecular Structure of 'Ruthenium Black' - Di- μ -amido-bis[tetraammineruthenium(III)] chloride Tetrahydrate," Michael T. Flood, Ronald F. Ziolo, Joseph E. Earley and Harry B. Gray, Inorg. Chem. **12**, 2153 (1973).

"Reduction of Co(III) Oxidants by Ti(III)," Mato Orhanovic and Joseph E. Earley, Inorganica Chimica Acta, **12**, L16 (1975), (in press).

"Kinetics of Reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and cis and trans $\text{Co}(\text{en})_2\text{Cl}_2^+$ by Ti(III)," Mato Orhanovic and Joseph E. Earley, accepted by Inorg. Chem.

"On Hydroxide-Ion-Induced Redox Reactions of Some Ruthenium, Rhodium, and Titanium Complexes," Joseph E. Earley, S. Zakir Ali, Luiz P. Bignetti, Purushothaman Chalilpoyil, Frederick A. Czulada and Mato Orhanovic, Proc. of the Internat. Conf. on Coord. Chem. 16, 3.12 (1974).

"A New Example of Linear-Free Energy Correlations for Inner-Sphere Redox Processes," Keith M. Davies and Joseph E. Earley, accepted by Inorg. Chem.

"Reactions of Ti(III)-Amino Acid Complexes with Chloro-Complex Oxidants," R. Grillo, C. Rowe and Joseph E. Earley, in preparation.

"Redox Trans Effects in Reduction of Co(III) Oxidants by Ti(III)," S. Zakir Ali and Joseph E. Earley, presented at the Symposium on Electron Transfer Reactions, American Chemical Society Meeting in Los Angeles, 1974. (in preparation)

"Kinetics of Reduction of Some Co(III) Complexes by Ti(III)," Purushothaman Chalilpoyil and Joseph E. Earley, to be presented at the 169th Meeting of the American Chemical Society in Philadelphia, in April, 1975. (in preparation)

"Reactivity Patterns Characteristic of Lighter Metallic Elements (Titanium)," Final Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Metallic elements such as titanium and aluminum are of specific Air Force interest as potential structural materials for use under extreme conditions. The use of these metals is limited by factors (stress corrosion, etc.) which depend directly on chemical reactivity.

This program has succeeded in clarifying many of the factors which contribute to the unusual reactivity patterns of titanium species in aqueous media.

It has established that interactions of Ti(III) with medium-anions are severe, and that this effect has caused serious errors in widely-quoted previous studies. In particular, rates for simpler oxidations of Ti(III) given in the literature are too high (due to medium interference) by three orders of magnitude. Unusual acid dependencies of Ti(III) reductions have been observed in several cases; these arise from the difference in geometry between predominant aqueous forms of titanium in trivalent and quadrivalent forms, and also from what appears to be a preference of Ti(III) for reductions through doubly-bridged binuclear complexes.

Originally, in this program the similarities of chemical properties between certain Ti(III) reactions and properties of ruthenium compounds were noted. The close relationship of Ti and Ru shows up in technically important reactions such as those of Ti-Ru alloy electrodes. A remarkable compound of Ru(III) has been discovered and characterized. This compound has a metal-metal bond and a bis- -amido doubly-bridged structure but yet has a triplet ground state. Papers have been published on both magnetochemical and structural studies of this compound and have pointed out that this structure seems likely to account for the unusual propensity of Ti(III) to react via di-bridged paths.

It has been shown that reactions of Ti(III) with simple oxidants (such as $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$) often involve singly-bridged electron transfer. Previous evidence on this point had been either inconclusive or erroneous. A stable

species which is an excellent model for the interactions which exist in such pathways is a ruthenium-containing trimer in which oxide ions join the ruthenium atoms and permit efficient interaction of metal ion orbitals. Although previous structural studies of such compounds have been inconclusive, it has been found that substitution of organic ligands for NH_3 has led to formation of tractable crystals. Both crystallographic and chemical characterization of species in this class have been published. The unusual reaction by which redox reactions of such species are induced by hydroxide ion have been shown to involve disproportionations of minor constituents of the preparations.

By study of redox reactions of more complex oxidants with Ti(III) , it was shown that the sensitivity of the free energy of activation of Ti(III) reactions to changes in free energy of reaction is lower than the sensitivity of oxidations of other common reductants. This is connected with the exceptional effectiveness of cross-bridge interactions for Ti(III) and Ru(III) , and contrasts with the behavior of Cr(II) - Co(III) which is now under study in this laboratory. Considerable progress has been made in extending these investigations to Ti(III) reactions.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Reactions Induced by Ultraviolet and Ionizing Radiation
2. PRINCIPAL INVESTIGATOR: Dr. George S. Hammond
Department of Chemistry
California Institute of Technology
Pasadena, California 91109
and
University of California (Santa Cruz)
Santa Cruz, California 95060
3. INCLUSIVE DATES: 1 July 1970 to 30 November 1974
4. GRANT NUMBERS: AFOSR-71-1958; AFOSR-73-2506
5. COSTS AND FY SOURCE: \$23,000 FY 70; \$50,000 FY 71
\$50,000 FY 72; \$34,000 FY 73
6. SENIOR RESEARCH PERSONNEL: Dr. Denis DeKeukeleire
Dr. Heniz Hefter
Dr. Dominic Labianca
Dr. Louisa Molina
Dr. Frank Quina
Dr. Gary Taylor
Dr. Shui Pong Van
7. JUNIOR RESEARCH PERSONNEL: Felix Carroll
Amitava Gupta
Takiko Fujisawa
John Winterle
8. PUBLICATIONS:

"Deactivation of Biacetyl Triplets by Cyanocobaltate (III) Complexes,"
M. Wrighton, D. Bredesen, G. S. Hammond and H. B. Gray, Chem. Comm.
1018 (1972).

"Rates of Termination of Radicals in Solution VI. Ketyl Radicals
Derived from Methyl Substituted Phenylglyoxylic Acids," T. Fujisawa
and G. S. Hammond, J. Amer. Chem. Soc. 94, 4175 (1972).

"Effects of a Magnetic Field on Some Photosensitized Reactions,"
A. Gupta and G. S. Hammond, J. Chem. Phys. 57, 1789 (1972).

"Multiple Mechanisms in the Thermal and Photochemical Decomposition
of 2,3-Diazabicyclo[3.1.0]hex-2-enes," D. F. Eaton, R. G. Bergman,
and G. S. Hammond, J. Amer. Chem. Soc. 94, 1351 (1972).

"Rates of Termination of Radicals in Solution. XVII Allylic Radicals,"
H. J. Hefter, C-H S. Wu and G. S. Hammond, J. Amer. Chem. Soc. 95,
851 (1973).

"Photochemical Reactivity of trans-Diacidotetracyanocobaltate(III)
Complexes," M. Wrighton, H. B. Gray, G. S. Hammond and V. Miskowski,
Inorg. Chem. 12, 740 (1973).

"Mechanisms of Photochemical Reactions in Solution. LXXVI. Complex Decay Mechanisms in Bi- and Trichromic Systems," D. DeKeukeleire, E. C. Sanford and G. S. Hammond, J. Amer. Chem. Soc. 95, 7904 (1973).

"Role of Charge Transfer Interactions in the Quenching of 1,4-Dimethoxybenzene Fluorescence," F. A. Carroll, M. T. McCall and G. S. Hammond, J. Amer. Chem. Soc. 95, 315 (1973).

"Case for Reactive Intermediates in the Interaction of Excited States of Ketones with Alkenes," A. Gupta and G. S. Hammond, J. Amer. Chem. Soc. 97, 254 (1975).

"Energy Wastage and Exciplex Formation in the Quenching of a Ketone Triplet by Sterically Hindered Alkenes," A. Gupta and G. S. Hammond, J. Amer. Chem. Soc., in press.

"Fluorescent Exciplexes Formed from Excited Naphthalenes and Tertiary Amines," S. P. Van and G. S. Hammond, in preparation.

"Delocalized Excited States in Arene-Amine Bichromophoric Compounds," F. H. Quina, L. Molina and G. S. Hammond, in preparation.

"Chemical Reactions Induced by Ultraviolet and Ionizing Radiation," G. S. Hammond, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this study involved five areas of research:

(1) the mechanism of production of electronically excited states by γ rays, (2) the properties of polar, fluorescent exciplexes, (3) nonradiative decay processes in the quenching of excited states, (4) studies of the kinetics of decay of free radicals produced photochemically, and (5) some early work in the photochemistry of organometallic compounds.

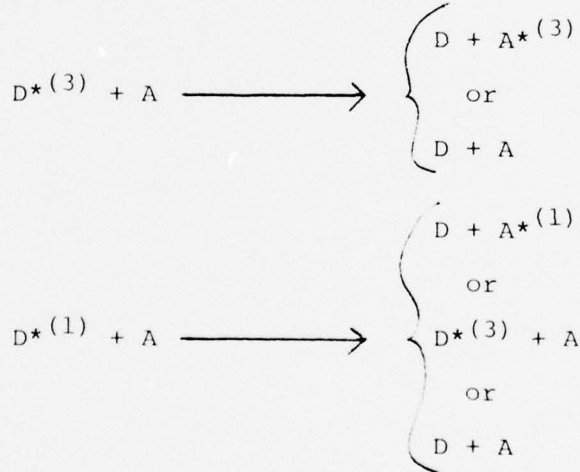
The radiation chemical studies used trans,trans-2,4-hexadiene ($\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_3$) as a monitor for singlet and triplet excitation generation in benzene solution. The key to the method is that excited singlet states of the diene, produced by direct irradiation, give only one-bond isomerization (i.e. tt \rightarrow ct) whereas triplet states produced by energy transfer from sensitizer triplets undergo two-bond isomerization (i.e. tt \rightarrow cc). The results indicated a surprisingly large contribution from single energy transfer to the solutes. The surprise was compounded by the demonstration that the fluorescent state of benzene is not quenched efficiently by the diene. A compelling argument was developed to the effect that the energy donor is a higher excited state of benzene, probably $^1\text{E}_{1\mu}$.

Study of fluorescent exciplexes produced by the encounter of the fluorescent states of naphthalene and its derivatives with tertiary amines has been going on for several years. A large number of bimolecular quenching systems were studied. The highlights of the work were (1) correlation of the energy of the exciplex emission with solvent polarizability in saturated hydrocarbon solution, (2) correlation of the transition moments for emission by a series of substituted naphthalenes and the exciplexes that they form with triethylamine. Both approaches are consistent with the view that

the exciplex has on the order of 90% "ionic character".

Three classes of bichromophoric amines were studied. In all cases the bichromophoric compounds have broad, structureless emissions at long wavelength which resemble closely the exciplex emissions produced by bimolecular interaction of the excited singlet state of naphthalene with amines. The emission frequencies show solvent dependence similar to that of bimolecular complexes. However, the quantum yield behavior is different. The rigid bichromophores have very low quantum yields for emission which vary little with solvent. Thus rigid compounds emit with much lower than maximum intensities observed with bimolecular exciplexes in hydrocarbon solvents but do still show some emission in polar solvents, like acetonitrile, in which there is no detectable exciplex emission in the bimolecular cases. It is known from the work of others that in polar solvents the exciplex decays by two different paths, to produce separated ion radicals and to produce naphthalene triplets. It was found that in two cases studied the bichromophoric arene-amines decay to give very high yields of triplets. This suggests some interesting theoretical conclusions which will be elaborated in a paper now in preparation.

Several pieces of work were done which were oriented toward study of nonradiative decay competing with electronic energy transfer, a process sometimes referred to as "energy wastage". Examples documented include the following general types:



It is noteworthy that many of the energy wastage reactions appear to include accelerated intersystem crossing (i.e. triplet + singlet \longrightarrow two singlets, or two singlets \longrightarrow singlet plus triplet).

A rather detailed study of isomerization of some sterically hindered alkenes with acetophenone triplets showed that in some cases energy wastage can become virtually the only observable path. By doing experiments in ternary systems (acetophenone-alkene-1,3-pentadiene) it was possible to show that triplet exciplexes are formed from acetophenone triplets and alkenes. The exciplexes were detected because they live long enough to be scavenged by 1,3-pentadiene (piperylene), a well known triplet getter.

Study of the kinetics of bimolecular decay of free radicals continued. Probably the most important work reported during the recent grant period was a study of the effects of temperature on the rates of recombination of several types of allylic radicals. The results, for the most part, were well accommodated by a model which interprets the influence of temperature as a viscosity effect.

Work with organometallic compounds centered on photosubstitution reactions of ground-state-nonlabile d^6 compounds and ions.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Electronically Excited Metal Atoms Produced by Chemical Reactions
2. PRINCIPAL INVESTIGATOR: Dr. J. L. Hirschfield
Department of Engineering and
Applied Science
Yale University
New Haven, Connecticut 06520
3. INCLUSIVE DATES: 1 January 1974 to 30 June 1975
4. GRANT NUMBER: AFOSR-74-2637
5. COST AND FY SOURCE: \$47,923 FY 74
6. RESEARCH PERSONNEL: Dr. Jacob Maya
Eric Lee

7. PUBLICATIONS:

"Chemiluminescence from Thallium-Fluorine Reactions," J. Maya and P. C. Nordine, J. Chem. Phys. 62, 1995 (1975).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The study of exoergic chemical reactions that produce light has been a fruitful area of research for many years. The chemiluminescence from these reactions provides basic information about the reaction mechanism. Recently there has been a renewed interest in these reactions motivated in part by developments in the field of chemical lasers. It has been shown that chemical lasers can be relatively efficient and can produce a large power output. However all chemical lasers developed so far operate in the infrared region of the spectrum. The long wavelength of these lasers limits their usefulness. It is hoped that some of the reactions that produce visible chemiluminescence may provide population inversion necessary for lasers in the visible wavelength range.

From the point of view of obtaining laser oscillations there is a definite advantage in studying reactions that lead to electronically excited atoms rather than excited molecules. In atoms there are far fewer excited states and therefore adequate inversion for laser action between two specific states is more likely. Furthermore since the electronic structure and properties of many excited atoms are well known the interpretation of experimental results may be easier.

A type of highly exoergic chemical reaction in which one of the reaction products is an electronically excited metal atom is the reaction of metal dimers with halogen atoms:



Where M and M* are respectively ground state and electronically excited metal atoms and X is a halogen atom. As an example a

spectroscopic study on the flame resulting from the reaction of thallium with fluorine was performed in a flow system. The chemiluminescence from this reaction was observed to produce thallium atomic emission at 3529, 3519, 3776 and 5350 angstroms. The electronic excitation of thallium seems to occur from reactions involving thallium dimer, atomic fluorine, vibrationally excited thallium fluoride and atomic thallium. No inversion of population in the excited atomic states was observed. The intensities of atomic emission can be characterized by a Boltzmann distribution with an electronic temperature of about 3000 degrees. Light emission is also observed from electronically excited thallium fluoride. An upper bound for the dissociation energy of thallium dimer was established to be 20 K cal per mole. These experiments indicate that the mechanism for the reaction of thallium dimer with halogen atoms is essentially the same as that for the reaction of the alkali metal dimers.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Non-Stoichiometric Oxides: Structure, Texture, Thermodynamics and Magnetic Properties
2. PRINCIPAL INVESTIGATOR: Dr. Bruce G. Hyde and
Dr. B. N. Figgis
Department of Chemistry
University of Western Australia
Nedland, Western Australia 6009
3. INCLUSIVE DATES: 1 May 1972 to 31 January 1975
4. GRANT NUMBER: AFOSR-72-2312
5. COSTS AND FY SOURCE: \$33,400 FY 72, \$24,333 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. A. N. Bagshaw
Dr. L. A. Bursill
Dr. F. J. Lincoln
7. JUNIOR RESEARCH PERSONNEL: M. O'Keeffe
D. K. Philip
8. PUBLICATIONS:

"The Thermodynamics of the Titanium + Oxygen System: An Isothermal Gravimetric Study of the Composition Range Ti_3O_5 to TiO_2 at 1304°K," R. R. Merritt and B. G. Hyde, Phil. Trans Roy. Soc. Lond. A 274, 627-661 (1973).

"On Mechanisms of the $B1 \longleftrightarrow B2$ Structural Transformation," B. G. Hyde and M. O'Keeffe, Phase Transitions, 345-349 (1973), ed. L. E. Cross, New York: Pergamon Press (1974).

"Twinning on the Unit Cell Level as a Structure Building Operation in the Solid State," Sten Anderson and B. G. Hyde, J. Solid State Chem. 9, 92-101 (1974).

"An Electron Microscope Study of the $FeO-Fe_2O_3-TiO_2$ System and of the Nature of Iron Doped Rutile," L. A. Bursill, J. Solid State Chem. 10, 72-94 (1974).

"Continuous Structure Variation and Rotating Reciprocal Lattices in the Titanium-Chromium Oxides," D. K. Philip and L. A. Bursill, Acta. Cryst., A 30, 265-272 (1974).

"Phase Analysis Studies of Titanium-Chromium Oxides Derived from Rutile by Crystallographic Shear," D. K. Philip and L. A. Bursill, J. Solid State Chem., 10, 357-370 (1974).

"Anion Coordination Geometry as a Determining Factor in Crystallographic Shear," B. G. Hyde, Nature 250, 411-412 (1974).

"Some Defect Structures in Crystalline Solids," B. G. Hyde, A. N. Bagshaw, Sten Anderson and M. O'Keeffe, Ann. Rev. Mater. Sci., 4, 43-92 (1974).

"Relationships Between the Structures of the Rare Earth Fluorides and High Chalcocite, Cu_2S . Implications for Solid Electrolyte Behaviour," M. O'Keeffe and B. G. Hyde, J. Solid State Chem., **13**, 172-175 (1975).

"Rutile: Planar Defects and Derived Structures. In Electron Microscopy in Mineralogy," B. G. Hyde, Berlin: Springer, in press.

"The Solid Electrolyte Transition and Melting in Salts," M. O'Keeffe and B. G. Hyde, Submitted to Phil. Mag.

"Relationships Between the Structures of Cristobalite and Related Compounds," M. O'Keeffe and B. G. Hyde, 33 pp. to be submitted probably to Acta Cryst.

"Plane Nets in Crystal Chemistry," M. O'Keeffe and B. G. Hyde, 180 pp. to be submitted to Phil. Trans. Roy. Soc. Lond.

The following are some of the publications in preparation:

"Ionic Crystals, Some Fundamental Principles," M. O'Keeffe and B. G. Hyde.

"Crystal Structures, a Monograph," Sten Anderson and B. G. Hyde.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The basic goal of this study was to produce realistic models for (a) disorder in single, binary, and inorganic solids, (b) non-stoichiometry, and (c) solid state reaction mechanisms. An assessment of theories of the solid state was to be made and experimental methods to be compared so that the most direct and informative techniques may be utilized.

The success of this approach to the structure problems in the solid state chemistry of transition metal oxides has been a cause of continual satisfaction to the investigators. It involved a reconsideration of known structures, which were correlated in various ways, together with a reappraisal of the basic, classical ideas on the crystal chemistry of ionic solids. In both cases novel, and somewhat revolutionary concepts are emerging. The thermodynamics of the titanium-oxygen system in the composition range of Ti_3O_5 to TiO_2 at 1304°K has been completed and published. Anion diffusion rates have been measured in titanium oxide single crystals. There seems to be no very marked trend in diffusion coefficient with composition. The technique involved oxygen isotope exchange between the solid and a water plus hydrogen gas buffer, followed mass-spectrometrically. A novel technique has been developed for studying oxidation/reduction mechanisms in transition-metal oxides by direct observation in the electron microscope. Studies of rutile related systems have been concluded with detailed examinations of the systems $\text{Cr}_2\text{O}_3 + \text{TiO}_2$ and $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{TiO}_2$. It revealed the phenomenon of "swinging CS planes" where, by rotation of the CS plane direction a continuous sequence of fully-ordered structures of varying composition is possible.

The structure and structural relationship study has broadened into a new approach to crystal chemistry, including inorganic, mineral and alloy structure. The complete work will be contained in the monograph "Crystal Structures" - Sten Anderson and B. G. Hyde.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: The Solid State Properties of Transition Metal Complexes.
2. PRINCIPAL INVESTIGATOR: Dr. Leonard Interrante
Dr. John Kasper
Research & Development Center
General Electric Company
Schenectady, New York
3. INCLUSIVE DATES: 1 September 1971 - 30 June 1975.
4. CONTRACT NUMBER: F44620-71-C-0129.
5. COSTS AND FY SOURCE: \$30,000 FY71; \$30,000 FY73; \$25,000 FY74; \$45,000 FY75
6. SENIOR RESEARCH PERSONNEL: Dr. K. W. Browall
Dr. J. W. Bray
Dr. F. P. Bundy
Dr. I. S. Jacobs
Dr. G. D. Watkins
7. JUNIOR RESEARCH PERSONNEL: None.
8. PUBLICATIONS:

"The Molecular Structure of Palladium and Platinum Bis(ethylene-1, 2-dithiolene). A Novel Metal-Metal Bonded Dimer", K. W. Browall, L. V. Interrante and J. S. Kasper, J. Amer. Chem. Soc., 93, 6289 (1971).

"Electron Delocalization in Metal Chain Complexes. Evidence for Extrinsic Conductivity in Magnus' Green Salt", L. V. Interrante, Chem. Comm. 302 (1972).

"The Absorption Spectrum of Magnus' Green Salt in the Near Infrared Region", E. Fishman and L. V. Interrante, Inorg. Chem. 11, 1722 (1972).

"The Crystal and Molecular Structure of Neutral Bis(ethylene-1, 2-dithiolene) Complexes of Pd and Pt. Evidence for Metal-Metal Bonding", K. W. Browall, T. Bursh, L. V. Interrante, and J. S. Kasper, Inorg. Chem. 11, 1800 (1972).

"The Electrical Conductivity of $K_2Pt(CN)_4Br_{0.3} \cdot 2.3 H_2O$ at Ultra-High Pressures", L. V. Interrante and F. P. Bundy, Solid State Comm., 11, 1641, (1972).

"Studies of Intermolecular Interactions in Planar Metal Complexes, III: Bis(ethylene-1-2-dithiolene) Complexes of Nickel, Palladium, and Platinum," K. W. Browall and L. V. Interrante, J. Coord. Chem. 3, 27 (1972).

"Studies of Intermolecular Interactions in Transition Metal Complexes, IV: A High Pressure Study of Some Mixed Valence Platinum and Palladium Complexes", L. V. Interrante, F. P. Bundy, and K. W. Browall, Inorg. Chem. 13, 1158 (1974).

"Studies of Intermolecular Interactions in Transition Metal Complexes, V: The Electrical Properties of Some Mixed Valence Platinum and Palladium Complexes", L. V. Interrante and K. W. Browall, Inorg. Chem. 13, 1162 (1974).

"The Unit Cells of PtX_3 (X=Cl, Br, I)", K. W. Browall, J. S. Kasper, and L. V. Interrante, Acta Crystallographica, 30B (1974).

"Electronic Structure of Square-Planar Transition Metal Complexes, I: The $PtCl_4^{2-}$ and $PdCl_4^{2-}$ Ions", R. P. Messmer, L. V. Interrante, and K. H. Johnson, J. Am. Chem. Soc., 96, 3847 (1974).

"The Electronic Structure of the $\text{Pt}(\text{CN})_4^{2-}$ Ion", L. V. Interrante and R. P. Messmer, Chem. Phys. Letters, 26, 225 (1974).

"A SCF-X α -SW Investigation of Solid State Interactions in $\text{Pt}(\text{CN})_4^{n-}$ Complexes", L. V. Interrante and R. P. Messmer, ACS Symposium Series 5, 382 (1974).

"Electron Transport in One-Dimensional Metal Complex Semi-conductors", L. V. Interrante, Proceedings of the NATO Advanced Study Institute on Low-Dimensional Cooperative Phenomena and the Possibility of High-Temperature Superconductivity, Plenum Publishing Corporation, New York, N.Y., 299, (1975).

"The Preparation and Properties of Some Tetrathiafulvalene Donor-Acceptor Compounds with Bis-Metal Complexes", L. V. Interrante, K. W. Browall, H. R. Hart, Jr., I. S. Jacobs, G. D. Watkins, and S. H. Wee, J. Amer. Chem. Soc., 97, 889, (1975).

"The Crystal Structure of $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$ ", J. S. Kasper, L. V. Interrante, and C. A. Secaur, J. Amer. Chem. Soc. 97, 4890 (1975).

"Electrical Property Studies of Planar Metal Complex Systems", L. V. Interrante Advances in Chemistry, 1975 (in press).

"Observation of a Spin-Peierls Transition in a Heisenberg Antiferromagnetic Linear Chain System", J. W. Bray, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, and J. C. Bonner, submitted to Phys. Rev. Lett.

"Effects of Copper (II) and Iron (II) Doping on the Bound Electronic States in the One-Dimensional Semiconductor Magnus' Green Salt", F. Mehran and L. V. Interrante, submitted to Solid State Communications.

"Solid State Properties of Transition Metal Complexes" L. V. Interrante and J. S. Kasper, Final Tech Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this research program was to generate an understanding of the relationship of the structural parameters and surface interactions of transition metal complexes to their solid-state properties and to utilize this behavior for predicting and controlling the properties of this class of materials. The approach chosen to meet these objectives consisted of selecting several representative types of transition metal complex systems where potentially interesting solid-state behavior has been previously identified and studying the electrical and magnetic properties of these systems as a function of structural variables accessible through either chemical substitution or the application of ultrahigh pressures. The work was focused on three main types of transition metal complexes; (1) the metal chain systems, $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4(\text{MGS})$ and $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}(\text{KCP})$; (2) the halide-bridged mixed valence complexes, $\text{M}(\text{A})_2\text{X}_2$ ($\text{M}=\text{Pd}, \text{Pt}$; $\text{A} = \text{NH}_3, \text{en}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$); and (3) the bis-dithiolate metal complexes $\text{R}_n^+(\text{MS}_4\text{C}_4\text{X}_4^{n-})$. The results of the studies of these systems are described in the publication listed above.

In this work, particular attention was paid to characterizing the role of the transition metal complex unit (i.e., its composition, molecular geometry, and electronic structure) and its arrangement in the solid in determining the solid-state properties. In addition to experimental studies, theoretical calculations in collaboration with Dr. R. P. Messmer of General Electric Corporate Research and Development, were carried out in order to obtain information concerning the electronic structure of the molecular units and the orbital interactions occurring in the solid.

Throughout this work, the importance of detailed structural information regarding the relative orientation and separation of the molecular units in the structure were fully recognized, and collaborative efforts with Dr. J. S. Kasper of General Electric Corporate Research and Development in the first three years of the program were of considerable value in meeting the objectives. As the focus of the program began to shift from studies of known complexes to the synthesis and characterization of new solid-state materials, this need for structural information became particularly acute. In recognition of this need, the program was expanded in September 1974 to formally include Dr. Kasper as a second principal investigator.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Collisional Energy Transfer and Other Topics Related to Gas Laser Mechanisms
2. PRINCIPAL INVESTIGATOR: Dr. A. Javan
Department of Physics
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 December 1972 to 31 December 1974
4. GRANT NUMBER: AFOSR-73-2475
5. COSTS AND FY SOURCE: \$32,500 FY 73; \$17,000 FY 74
\$17,000 FY 75
6. SENIOR RESEARCH PERSONNEL: Dr. H. L. Chen
Dr. B. M. Hopkins
Dr. R. H. Picard
Dr. L. Poulsen
Dr. H. Schlossberg
Dr. R. D. Sharma

7. PUBLICATIONS:

"On the Assumptions Underlying the Near-Resonant Theory of Energy Transfer," R. D. Sharma and H. Schlossberg, Chem. Phys. Letrs. 20, 5 (1973).

"Temperature Dependence of Near Resonant Vibration \rightarrow Vibration Energy Transfer in HCl-D₂ Mixtures," B. M. Hopkins, Hao-Lin Chen and R. D. Sharma, J. Chem. Phys. 59, 5758 (1973).

"Vibration-to-Vibration Energy Transfer in Collisions between H³⁵Cl and H³⁷Cl," R. D. Sharma, Chem. Phys. Letrs. 24, 267 (1974).

"Collision-Induced Absorption in He-Ne Mixture," R. D. Sharma and R. R. Hart, Chem. Phys. Letrs. 27, 589 (1974).

"Temperature Dependence of Near-Resonant Vibration \leftrightarrow Rotation Energy Transfer," D. Frankel, J. I. Steinfeld, R. D. Sharma and L. Poulsen, Chem. Phys. Letrs. 28, 485 (1974).

"Vibration-to-Vibration Energy Transfer in CO-CO Collisions," R. D. Sharma, Chem. Phys. Letrs. 30, 261 (1975).

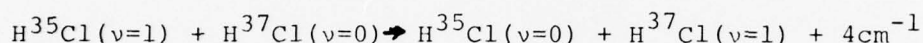
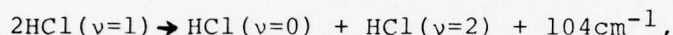
8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Through the period of the grant the work done represented important steps in the theory of energy transfer during molecular collisions and the theory of collision-induced absorption. The highlights of the work done are:

1. On The Assumptions Underlying The Near-Resonant Theory of Energy Transfer - An expression for the energy transfer cross section in the distorted-wave first-order Born approximation (DWFOBA) is

2. Temperature Dependence of Near Resonant Vibration \rightarrow Vibration Energy Transfer in HCl-D₂ Mixtures - Laser-excited vibrational fluorescence measurements have given rates for nearly resonant vibrational energy exchange between HCl and D₂ molecules over the temperature range of 196-343°K.

3. Vibration-to-Vibration Energy Transfer in Collisions Between H³⁵Cl and H³⁷Cl - The observed difference in the rates of energy transfer processes



is explained on the hypothesis that isotopic interactions play an important role in the second process whereas they are inoperative for the first process. This hypothesis, if true, gives an estimate of the derivative of the average quadrupole polarizability with respect to internuclear distance.

4. Calculations for the collision-induced absorption in a He-Ne mixture in the far infrared (200-600cm⁻¹) are presented. The present calculation includes an exact treatment of the collision dynamics and of the radiation field to the first order. The information used is the interatomic potential and dipole moment function. Using values of these parameters obtained from independent and extensive studies, values of the absorption coefficient are obtained which are about two orders of magnitude smaller than obtained previously.

5. Temperature Dependence of Near-Resonant Vibration \leftrightarrow Rotation Energy Transfer - V \leftrightarrow R,T deactivation of the v₄ (243cm⁻¹) level in BCl₃ by HCl has been measured over the range of 220-340K, with an infrared double resonance technique. The deactivation probabilities show an inverse temperature dependence below room temperature, indicating that long-range attractive forces are important in the resonant transfer process. The results are compared with the theory of Sharma and Brau.

6. Vibration-to-Vibration Energy Transfer in CO-CO Collisions - Vibration-to-vibration energy transfer rates for collision between two CO molecules are calculated. Results obtained are compared with recent experiments and theoretical values. It is pointed out that none of the existing calculations gives a complete account of the available experimental data.

7. Distorted-Wave Born Calculation of Near-Resonant Energy Transfer - The distorted-wave Born calculation for transfer of one quantum of asymmetric stretch from CO₂ to N₂¹⁴ and N₂¹⁵ is presented. A spherically symmetric Lennard-Jones 6-12 potential with parameters derived from transport properties is used as distorting potential. The energy transfer is assumed caused by dipole-quadrupole coupling, i.e. interaction involving the transition dipole of CO₂ and the transition quadrupole of N₂. The results obtained are in excellent agreement with those obtained earlier using a straight path as the trajectory during the intermolecular collision and an empirical recipe for summing over impact parameters.

8. Collision Induced Absorption in He-Ar Mixture - The absorption coefficient for the collision induced absorption (CIA) in a He-Ar mixture is calculated for frequencies between 67cm^{-1} - 733cm^{-1} in the $200\text{-}400^\circ\text{K}$ temperature range. Starting with a Lennard-Jones (6-12) interatomic potential derived from atomic beam work, the absorption coefficient is computed for five different dipole moment functions.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Transition Metal and Lanthanide Compounds
2. PRINCIPAL INVESTIGATOR: Dr. R. B. King
Department of Chemistry
University of Georgia
Athens, Georgia 30602
3. INCLUSIVE DATES: 1 January 1971 to 30 June 1975
4. GRANT NUMBER: AFOSR-71-2000
5. COSTS AND FY SOURCE: \$44,981 FY 71; \$48,176 FY 72; \$36,000 FY 73
\$45,744 FY 74; \$33,000 FY 75
6. SENIOR RESEARCH PERSONNEL: Dr. A. Bond
Dr. D. M. Braitsch
Dr. J. C. Cloyd, Jr.
Dr. J. W. Howard, Jr.
Dr. P. N. Kapoor
Dr. D. P. McDonald
Dr. R. H. Reimann
Dr. W. Z. M. Rhee
Dr. M. S. Saran
7. JUNIOR RESEARCH PERSONNEL: P. R. Heckley
P. K. Hendrick
K. C. Hodges
M. E. Norins
J. A. Zinich
8. PUBLICATIONS:

"P,P-Diphenylethylenediphosphine," R. B. King and Pramesh N. Kapoor, Angew. Chem. 83, 766 (1971), Angew. Chem. Int. Ed., 10, 734 (1971).

"Polytertiary Phosphines and Arsines. VII. Zerovalent Platinum Complexes of Arylated Polytertiary Phosphines and Arsines," R. B. King and Pramesh N. Kapoor, Inorg. Chem. 11, 1524 (1972).

"Isocyanide Metal Complexes. I. Reactions of the Pentakis-(tert-butylisocyanide)cobalt Cation with Some Tertiary Phosphines and Arsines," R. B. King and M. S. Saran, Inorg. Chem. 11, 2112 (1972).

"Novel Redox Systems in Hexamethylbenzene Metal Cluster Compounds of Niobium and Tantalum," R. B. King, D. M. Braitsch and Pramesh N. Kapoor, Chem. Comm., 1072 (1972).

"New Polyphosphines Containing Various Combinations of Primary, Secondary, and Tertiary Phosphorus Atoms," R. B. King and J. C. Cloyd, Jr. Z. Naturforsch. 27b, 1432 (1972).

"Polytertiary Phosphines and Arsines. VI. Some Metal Complexes of the Mixed Phosphine-Diarsine Bis(2-Diphenylarsinoethyl)-phenylphosphine," R. B. King and Pramesh N. Kapoor, Inorganica Chimica Acta. 6, 391 (1972).

"Novel Products from Reaction between Allyliron Tricarbonyl Iodide and Polypyrazolylborate Salts: A New Type of Allyl-Propenyl Isomerization," R. B. King and A. Bond, J. Organometal. Chem. **46**, C53 (1972).

"The Syntheses and Properties of Novel Polyphosphines Containing Various Combinations of Primary, Secondary and Tertiary Phosphorus Atoms," R. B. King, J. C. Cloyd, Jr. and P. N. Kapoor J. Chem. Soc. Perkin I, 2226 (1973).

"Polytertiary Phosphines and Arsines. VIII. Oxides and Sulfides of the Simple Polytertiary Phosphines," R. B. King and P. R. Heckley, Phosphorus **3**, 209 (1974).

"Polytertiary Phosphines and Arsines. IX. Polytertiary Phosphines with Five, Seven, Eight, and Ten Phosphorus Atoms," R. B. King and J. C. Cloyd, Jr., Phosphorus **3**, 213 (1973).

"Sulfurization as a Means for the Protection of Trivalent Phosphorus Atoms in the Syntheses of Methylated Polytertiary Phosphines," R. B. King, J. C. Cloyd, Jr. and Pamela K. Hendrick, J. Am. Chem. Soc. **95**, 5083 (1973).

"Isocyanide-Metal Complexes. II. CO and CN Stretching Modes in tert-Butyl Isocyanide Derivatives of the Octahedral Metal Carbonyls," R. B. King and M. S. Saran, Inorg. Chem. **13**, 74 (1974).

"Isocyanide-Metal Complexes. III. Reactions of tert-Butyl Isocyanide with Cyclopentadienylmolybdenum Carbonyl Derivatives," R. B. King and M. S. Saran, Inorg. Chem. **13**, 364 (1974).

"Metal Polypyrazolylborate Complexes. I. Reactions of Perfluoroalkyl-metal Carbonyl Halides of Iron and Cobalt with Polypyrazolylborates," R. B. King and A. Bond, J. Am. Chem. Soc. **96**, 1334 (1974).

"Metal Polypyrazolylborate Complexes. II. Reactions of Trimethylplatinum Derivatives with Polypyrazolylborates," R. B. King and A. Bond, J. Am. Chem. Soc. **96**, 1338 (1974).

"Metal Polypyrazolylborate Complexes. III. Reactions of Allyliron Tricarbonyl Iodide with Polypyrazolylborates," R. B. King and A. Bond, J. Am. Chem. Soc. **96**, 1343 (1974).

"Metal Polypyrazolylborate Complexes. IV. Some Reactions of Organometallic Rhodium (I) Chloride Derivatives with Polypyrazolylborates," R. B. King and A. Bond, J. Organometal Chem. **73**, 115 (1974).

"Lanthanide Nitrate Complexes of Some Macrocyclic Polyethers," R. B. King and Paul R. Heckley, J. Am. Chem. Soc. **96**, 3118 (1974).

"The Addition of Phosphorus-Hydrogen and Arsenic-Hydrogen Bonds to Vinyl Isocyanide," R. B. King and A. Efraty, J. Chem. Soc. Perkin I, 1371 (1974).

"Isomerism in the Linear Tetratertiary Phosphine 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane," R. B. King, P. R. Heckley and J. C. Cloyd, Jr., Z. Naturforsch. **29b**, 574 (1974).

"Isocyanide-Metal Complexes. IV. Reactions of Allylbis(acetonitrile) chlorodicarbonylmolybdenum with Various Isocyanides," R. B. King and M. S. Saran, Inorg. Chem. 13, 2453 (1974).

"Some 1:1 Base-Catalyzed Addition Reactions of Compounds Containing Two or More Phosphorus-Hydrogen Bonds to Various Vinylphosphorus Derivatives," R. B. King and J. C. Cloyd, Jr., J. Am. Chem. Soc. 97, 46 (1975).

"Polytertiary Phosphines and Arsines. X. The Syntheses of Methylated Polytertiary Phosphines," R. B. King and J. C. Cloyd, Jr., J. Am. Chem. Soc. 97, 53 (1975).

"Organometallic Chemistry of the Transition Metals. XXX. Redox Systems in Hexamethylbenzene Cluster Compounds of Niobium and Tantalum," R. B. King, D. M. Braitsch and P. N. Kapoor, J. Am. Chem. Soc. 97, 60 (1975).

"Carbon-13 N.M.R. Spectra of Some Polyphosphines with Ethane Bridges Between Trivalent Phosphorus Atoms," R. B. King and J. C. Cloyd, Jr., accepted for publication in J. Chem. Soc. Perkin II.

"Polytertiary Phosphines and Arsines. XI. Phosphorus-31 N.M.R. Studies on Some Metal Complexes of Polytertiary Phosphines," R. B. King and J. C. Cloyd, Jr., Inorg. Chem. 14, 1550 (1975).

"Polytertiary Phosphines and Arsines. XII. Some Metal Complexes of Methylated Ditertiary and Tritertiary Phosphines," R. B. King, J. A. Zinich, and J. C. Cloyd, Jr., Inorg. Chem. 14, 1554 (1975).

"Polytertiary Phosphines and Arsines. XIII. Some Neopentyl Polytertiary Phosphines," R. B. King, J. C. Cloyd, Jr., and R. H. Reimann, submitted for publication in J. Org. Chem.

"Complexes of Trivalent Phosphorus Derivatives. XVIII. Some Complexes of Neopentylphosphines with Rhodium, Nickel, and Palladium Chlorides," R. B. King, J. C. Cloyd, Jr., M. E. Norins and R. H. Reimann, submitted for publication in Inorg. Chem.

"Polytertiary Phosphines and Arsines. XIV. Some Metal Complexes of Neopentyl Polytertiary Phosphines," R. B. King, J. C. Cloyd, Jr., and R. H. Reimann, submitted for publication in Inorg. Chem.

"Mass Spectra of Some Neopentylphosphorus Derivatives," R. B. King, J. C. Cloyd, Jr. and R. H. Reimann, submitted for publication in Organic Mass Spectrometry.

"Complexes of Trivalent Phosphorus Derivatives. XVII. Reactions of Iron Carbonyls with 1,2,3-Triphenyl-1,2,3-Triphosphaindane," R. B. King and R. H. Reimann, submitted for publication in J. Am. Chem. Soc.

"Transition Metal and Lanthanide Compounds," R. B. King, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original objective of this research program was the development of basic transition metal and lanthanide chemistry in areas potentially

useful for fuel cell, superconductor, and laser technology. In connection with fuel cell technology, transition metal compounds with unusual redox properties or those capable of catalyzing reactions of oxygen with fuels were of particular interest. Consideration of this ultimate application led to the development of novel transition metal chemistry of organophosphorus, polypyrazolylborate, and alkyl isocyanide ligands as well as new methods for the synthesis of organophosphorus compounds of types suitable for coordination to transition metals. Some of the organophosphorus compounds synthesized during the course of this research program were also of interest as antioxidants in aircraft lubricating fluids. Consideration of the need for new approaches to superconducting materials led to the development of some new chemistry of hexamethylbenzene derivatives of niobium and tantalum. Consideration of the need for new laser materials led to the discovery of new lanthanide coordination compounds of macrocyclic polyethers as well as a new method for lanthanide separation based on selective adsorption on a macrocyclic polyether column.

The results of this work can be grouped into the following major areas: (a) new organophosphorus derivatives and their metal complexes, (b) polypyrazolylborate metal complexes, (c) isocyanide metal complexes, (d) niobium and tantalum chemistry, and (e) lanthanide chemistry. The research is described in detail in the listed publications.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Inorganic Photoelectron Spectroscopy Mass Spectrometry and Thermochemistry Related to Fields
2. PRINCIPAL INVESTIGATOR: Professor M. F. Lappert
Dr. J. B. Pedley
The School of Molecular Sciences
University of Sussex
Brighton, BN1 9QJ, ENGLAND
3. INCLUSIVE DATES: 1 January 1972 - 31 December 1974
4. GRANT NUMBER: AFOSR-72-2220
5. COSTS AND FY SOURCE:
6. SENIOR RESEARCH PERSONNEL: Dr. S. S. Krishnamurthy
Dr. M. R. Litzow
Dr. T. R. Spalding
Dr. J. S. Poland
7. JUNIOR RESEARCH PERSONNEL: J. C. Baldwin S. G. Gibbons R. Pearce
R. Boschi D. H. Harris W. Schmidt
J. D. Cotton A. Hudson G. J. Sharp
C. S. Cundy G. H. King N. C. Westwood
P. J. Davidson P. W. Lednor B. T. Wilkins
M. J. Doyle B. K. Nicholson
8. PUBLICATIONS:

"Bonding Studies of Compounds of Boron and the Group IV Elements. Part VII. Heats of Hydrolysis Bond Energies for some Trimethylmetallyl Derivatives $\text{Me}_3\text{M-X}$ ($\text{M}=\text{Si}, \text{Ge}$, and Sn)", J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. S. Poland, J. Chem. Soc. (Dalton), 1943(1972).

"CATCH Table 'Nitrogen Compounds'" J. P. Pedley, et al., Thermochem. Data 1972.

"CATCH Table 'Phosphorus Compounds' " J. B. Pedley, et. al., Thermochem. Data 1972.

"CATCH Table 'Silicon Compounds' " J. B. Pedley, et.al., Thermochem. Data 1972.

"CATCH Table 'Halogen Compounds' ", J. B. Pedley, et. al., Thermochem. Data 1972.

"Bonding Studies of Compounds of Boron and the Group IV Elements. Part IX. Photoelectron Spectra and Bonding Studies of Halogeno-, Dimethylamino-, and Methylboranes, BX_3 and BX_2Y ", G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, Faraday Disc. of the Chem. Soc., 1972, No. 54.

"Mass Spectrometry of Inorganic and Organometallic Compounds", M. F. Lappert, (Ed.) M. R. Litzow and T. R. Spalding, Elsevier, Amsterdam, (1973).

"Bonding Studies of Compounds of Boron and the Group IV Elements. X. Photoelectron Spectra of Compounds Me_4M ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$, or Pb) and the Lack of Participation of M d-orbitals ", R. Boschi, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, J. Organometallic Chem., 50, 69 (1973).

"Bonding Studies of Compounds of Boron and the Group IV Elements. Part XI. Photoelectron Spectra of Strained Cyclic Organosilicon Compounds", C. S. Cundy, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, J. Organometallic Chem., 51 99 (1973).

"Stable Homoleptic Metal Alkyls", P. J. Davidson, M. F. Lappert, and R. Pearce, Accounts Chem. Res., **7**, 209 (1974).

"CODATA Task Group on Key Values for Thermodynamics. Part IV", J. B. Pedley, et. al., International Council of Scientific Unions (1974).

"Activation Parameters for Rotation about an M-C Bond from Temperature Dependent ¹H n.m.r. Spectra of Rh Carbene Complexes", carb M. J. Doyle and M. F. Lappert, J. Chem. Soc. Chem. Comm., 679 (1974).

"Bonding Studies of Compounds of Boron and the Group III and IV Elements. XII. Variable Temperature He(I) Photoelectron Spectra of Group III Halides, 2MX₃ = M₂X₆ (M=Al or Ga; X = Cl, Br, or I)", M. F. Lappert, J. B. Pedley, G. J. Sharp and N. C. Westwood, J. Elec. Spec. and Rel. Phen., **3**, 237 (1974).

"Bonding Studies of Transition Metal Complexes. He(I) Photoelectron Spectra of d⁰ Silylmethyl and Neopentyl Derivatives of Group IVA Metals", M. F. Lappert, J. B. Pedley, and G. J. Sharp, J. Organometallic Chem., **66**, 271 (1974).

"Photochemical Synthesis and e.s.r. Characterisation of Stable Trivalent Metal Alkyls (Si, Ge, Sn) and Amides (Ge and Sn) of Group IV Elements", J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert and P. W. Lednor, J. Chem. Soc. Chem. Comm., 651 (1974).

"Homolysis of Metal-Carbon and Metal-Metal Bonds: Spin-Trapping of the Resulting Carbon- and Metal-Centred Radicals", A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, J. Chem. Soc. Chem. Comm., 966 (1974).

"CODATA Recommended Key Values for Thermodynamics, 1973", J. B. Pedley, et.al., J. Chem. Thermodynamics, **7**, 1 (1975).

"Binuclear Organometallic Compounds. Part IX. Nuclear Magnetic Double Resonance Studies of Tin-119 Chemical Shifts in Compounds with Transition Metal-to-Tin-Bonds", D. H. Harris, M. F. Lappert, and J. S. Poland, J. Chem. Soc. (Dalton), 311 (1975).

"Bonding Studies of Transition Metal Complexes. Part II. Helium-I Photoelectron Spectra of Homoleptic d⁰, d¹, and d¹⁰ tetrakis(dialkylamides) of Transition and Group IVB Metals and Tungsten Hexakis(Dimethylamide)", S. G. Gibbins, M. F. Lappert, J. B. Pedley, and G. J. Sharp, J. Chem. Soc. (Dalton), 72, (1975).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research involved the study of the bonding and thermochemistry of simple compounds of boron and the Group IV Elements silicon, germanium and tin. Values were obtained for valence shell electrons by mass spectrometric ionization potential and photoelectron spectroscopy, binding energies of inner orbitals by X-ray excitation photoelectron spectroscopy (ESCA), standard heats of formation and thermochemical bond energy terms with a rotating bomb calorimeter, bond dissociation energies, redistribution reaction equilibrium constants and thermodynamic and spectroscopic parameters by NMR, NQR and magnetic circular dichroism.

Thermodynamic, kinetic, and spectroscopic data of various types have been gathered and are relevant to interpretations of bonding and stability of compounds related to important structural materials, including glasses and polymers and to potential high energy fuels.

Measurements were made of heats of hydrolysis of numerous compounds of the type $\text{Me}_3\text{M-X}$ [$\text{Me} = \text{CH}_3$; $\text{M} = \text{Si, Ge, or Sn}$; and $\text{X} = \text{Cl, Br, I, OMe, SC}_4\text{H}_9\text{-n, NMe}_2, \text{NMe}(\text{MMe}_3), \text{N}(\text{MMe}_3)_2, \text{and NH}(\text{MMe}_3)$]. From these data, standard heats of formation were obtained, and calculations led to the thermochemical bond energy terms $E(\text{M-Hal}), E(\text{M-O}), E(\text{M-S})$ and $E(\text{M-N})$. The results are of interest in connection with Group trends and questions of $\text{M-X } d\pi-p\pi$ bonding, as well as of the relative "hardness" or "softness" of the ions Me_3M^+ .

Measurements were made of heats of combustion of simple silicon compounds, such as $(\text{Me}_3\text{Si})_2\text{O}$, Me_6Si_2 , and Et_4Si . A rotating-bomb calorimeter was constructed and worked satisfactorily.

Measurements of first ionisation potentials of all the twenty boron halides $\text{BXX}'\text{X}''$ and of other simple boron compounds was carried out mass spectrometrically and the results analysed by quantum mechanical methods.

Measurements of ^{11}B nuclear magnetic spectra for $\text{BXX}'\text{X}''/\text{BYY}'\text{Y}''$ systems. These have provided equilibrium constants for redistribution and $^{11}\text{B}/^{19}\text{F}$ coupling constants.

Measurements of photon-excitation photoelectron spectra were made for simple compounds of $\text{BXX}'\text{X}''$. This study provided the energies of the four or five highest occupied orbital energy levels and their assignments according to symmetry and bonding.

Measurements of photon-excitation photoelectron spectra were made for simple Group III compounds $2\text{MX}_3 \rightleftharpoons \text{M}_2\text{X}_6$ ($\text{M} = \text{Al, Ga, or In}$; $\text{X} = \text{Cl or Br}$) have been carried out at various temperatures. This has allowed the spectra both of monomers and dimers to be recorded.

Measurements of photon-excitation photoelectron spectra were made for simple derivatives of silicon, phosphorus, and also of other Group IV elements, and of transition metals.

Measurements were made of X-ray-excitation photoelectron spectra of some simple boron compounds, such as $\text{B}(\text{OH})_3$, NaBF_4 . In this study, the $1s$ boron orbital binding energy was examined as a function of ligands, charge, and co-ordination number.

Measurements were made of ^{119}Sn Mossbauer spectra of organotin compounds, particularly those of formula $\text{Me}_3\text{Sn-X}$; of special interest have been compounds having tin-metal bonds.

Heteronuclear double resonance and 'Indor' spectra were used to obtain ^{119}Sn chemical shifts, and where appropriate, coupling constants for the organotin compounds. Exceptionally low-field chemical shifts in species with light transition metal atoms are attributed to a large paramagnetic contribution arising from small average excitation energies associated with $d\pi-d\pi$ bonding.

Electron spin resonance (e.s.r.) spectra have been used to characterize the unusually stable trivalent metal alkyls (Si, Ge, or Sn) and amides (Ge or Sn) of formulae $\text{M}[\text{CH}(\text{SiMe}_3)_2]_2$ and $\text{M}[\text{N}(\text{SiMe}_2)_3]$.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Kinetics of Selected Fluorine Reactions
2. PRINCIPAL INVESTIGATOR: Dr. J. B. Levy
Department of Chemistry
The George Washington University
Washington, DC 20052
3. INCLUSIVE DATES: 1 September 1970 to 31 August 1974
4. GRANT NUMBER: AFOSR-70-1939
5. COSTS AND FY SOURCE: \$20,050 FY 70; \$22,125 FY 71
\$24,822 FY 73; \$25,179 FY 74
6. RESEARCH PERSONNEL: R. C. Kennedy
7. PUBLICATIONS:

"Bistrifluoromethyl Peroxide. I. Thermodynamics of the Equilibrium with Carbonyl Fluoride and Trifluoromethyl Hypofluorite," J. B. Levy and R. C. Kennedy, J. Am. Chem. Soc. 94, 3302 (1972).

"Bistrifluoromethyl Peroxide. II. Kinetics of the Decomposition to Carbonyl Fluoride and Trifluoromethyl Hypofluorite," R. C. Kennedy and J. B. Levy, J. Phys. Chem. 76, 3480 (1972).

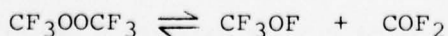
"Homolytic Displacements on Carbon. I. The Fluorine-Perfluorocyclobutane Reaction," J. B. Levy and R. C. Kennedy, J. Am. Chem. Soc. 96, 4791 (1974).

"The Pyrolysis of Hexafluoropropylene Oxide," J. B. Levy and R. C. Kennedy, submitted.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

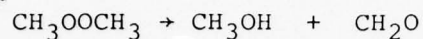
The focus of the research has been on the chemistry of fluorine and its compounds. The unique nature of fluorine manifests itself in the high reactivity of the element itself and in the interesting and unusual properties that fluorine imparts to compounds when it is incorporated in them. Both of these aspects are pertinent to the interests of the U.S. Air Force in that fluorine itself and fluorine-containing compounds are capable of acting as ingredients of high energy propellants on the one hand, and also yield lubricants, insulators, etc. of great chemical inertness on the other hand.

The research covered in this program falls rather naturally into two parts. The first part of the research dealt with the interesting equilibrium:



Rather profound effects of fluorine substitution have been noted. Measurements of the thermodynamic properties of the above system have been performed. It is interesting that the corresponding

reaction for the hydrogen analog:



is not an equilibrium, but an irreversible reaction. The particular nature of fluorine, among others, the relative weakness of its bond to oxygen, results in a reversible nature to the reaction which in turn leads to a particular stability of the perfluorinated peroxide since it has no easy route to destruction. A second effect of fluorine, illustrated in the above case, is its effect on other bonds in molecules in which it is incorporated. In the above case the result is a substantially increased oxygen-oxygen bond in the peroxide.

The second phase of research has been involved with the little-studied homolytic bimolecular substitution reaction, designated $\text{S}_\text{H}2$. A consequence of the strong bond that fluorine forms to carbon and the weak one that it forms with itself is that the reaction of fluorine with fluorocarbons is peculiarly well-suited to the study of $\text{S}_\text{H}2$ reactions.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Structure and Properties of Glasses under High Pressures as Related to Structural, Optical and Electronic Materials
2. PRINCIPAL INVESTIGATOR: Dr. John D. Mackenzie
Materials Department
University of California, Los Angeles
Los Angeles, California 90024
3. INCLUSIVE DATES: 1 September 1969 - 31 August 1974
4. GRANT NUMBER: AFOSR-70-1856
5. COSTS AND FY SOURCES: \$28,369 FY70; \$42,641 FY73;
33,412 FY71; 35,215 FY74
41,312 FY72;
6. SENIOR RESEARCH PERSONNEL: Dr. A. Makinshima, Dr. M. Yamane
7. JUNIOR RESEARCH PERSONNEL: K. Park, J.D. Johnson, D.S. Postupack
J. Wakaki, J. Ericson
8. PUBLICATIONS:

"Preparation and Properties of Non-Crystalline Films", J. Vac. Sci. Tech.,
6, 658-662 (1959), J. D. Mackenzie

"Vapor Phase Formation of Non-Crystalline Films by a Microwave Discharge
Technique", Chap. 18, p. 242-249, Chemical Reactions in Electrical Dis-
charges, Advances in Chemistry Series 80, American Chem. Soc. (1969),
J. D. Mackenzie and D. R. Secrist.

"Suppression of the Semiconductor - Metal Transition in Vanadium Oxide",
J. Non-Crystalline Solids, 1, 326-330 (1969) T. N. Kennedy and J. D.
Mackenzie.

"Electronic Conduction in Non-Crystalline Solids", J. Non-Crystalline Solids,
2, 16-26 (1970), J. D. Mackenzie

"Effects of Impurities on the Electrical Conductivity of Glassy Selenium",
J. Non-Crystalline Solids, 3, 234-236 (1970) W. C. LaCourse, V.A.Twadell
and J. D. Mackenzie

"Model for Self-Trapping Controlled Hole Transport in Trigonal Selenium",
Physical State Solids, 42, K167-170 (1970) W. C. LaCourse and J. D. Mackenzie

"Corrosion of Refractory Metals by Molten Oxides", Glass Industry, 51, 454-458
(1970) by G. A. Pecoraro, J. D. Mackenzie and H. Franz

"Structure and Electronic Properties of Amorphous Oxide Films", Proc. Int. Cong.
Thin Films, Cannes, France, 276-286, (1970) J. D. Mackenzie

"Semiconducting Glasses" in: Physics of Electronic Ceramics, Ed by Hench and
Dove, Marcel Dekker, Inc., New York, Chap 6 (1971) J. D. Mackenzie

"Relation between Apparent Glass Transition Temperature and Liquidus Temperature for Inorganic Glasses", J. Non-Crystalline Solids, 6., 145-162, (1971) S. Sakka and J. D. Mackenzie

"Effects of High Pressure on Solid and Molten Glass", Frontiers of Glass Science and Technology, Ed. by S. Bateson and A. Sadler, Canadian Ceram. Soc. Proc. 165-167, (1971), J. D. Mackenzie.

"Glass Bonded Composites of Practical Interests", Proc. of IX Int'l Conf on Mechanical Behavior of Materials, Vol IV, 347-359 (1972), J. D. Mackenzie

"Impurity Effects on the Structure and Electrical Properties of Non-Crystalline Selenium" J. Non-Crystalline Solids, 8-10, 831-836 (1972) W. C. LaCourse, V. Twadell, and J. D. Mackenzie

"Phototropic Glasses Activated by TiCl_4 ", J. Amer. Ceram. Soc. 55, 553-557 (1972) S. Sakka and J. D. Mackenzie

"Conductivity of Glasses and other Amorphous Solids, in Electrical Conductivity in Ceramics and Glass, Ed. by N. M. Tallan, Marcel Dekker, Inc., New York, Chap 8 (1972) J. D. Mackenzie.

"Photochromism of Thallium Chloride", Bull. Chem. Soc. Japan, 46, 848-851, (1973) S. Sakka and J. D. Mackenzie.

"Direct Calculation of Young's Modules of Glass", J. Non-Crystalline Solids, 12, 35-45 (1973) A. Makishima and J. D. Mackenzie.

"Secondary Electron Emission from Glass and its Practical Applications", J. Non-Crystalline Solids, 12, 1-17 (1973) K. Ooka, B. Dunn and J. D. Mackenzie

"Foamed Glass and Tiles from Waste Containers", Proc. Symposium on Utilization of Waste Glass, Univ of N. Mexica, 293-303 (1973) J. D. Mackenzie.

"Secondary Electron Emission of Semiconducting Glasses", J. Am. Ceram. Soc., 56, Sept. (1973) B. Dunn, K. Ooka and J. D. Mackenzie.

"Vicker's Hardness of Glass", J. Non-Crystalline Solids, 15, 153-164 (1974), M. Yamane and J. D. Mackenzie.

"Development of Glasses for Some New Applications", Proc. Tenth Int. Cong. of Glass, 4, 71-81, (1974) J. D. Mackenzie.

"Preparation of Low Dielectric Constant Glasses", J. Non-Crystalline Solids, 16, 313-314 (1974), B. Dunn, F. Chen and J. D. Mackenzie.

"Single Bond Strength for GeO_2 Glass", J. Non-Crystalline Solids, 16, 315-315 (1974) A. Makishima

"Chemical and Physical Properties of Obsidian: A Naturally-Occurring Glass", J. Non-Crystalline Solids, accepted for publication, A. Makishima and J. D. Mackenzie

"Thermal Expansion of Glasses", J. Non-Crystalline Solids, submitted for publication by A. Makishima and J. D. Mackenzie

"Preparation of Hard Glass", in report form, await clearance for publication by Khee Park, A. Makishima, M. Yamane and J. D. Mackenzie.

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Glasses are solids with no long-range order. Direct tools to obtain structural information such as x-ray diffraction are inadequate. In order to predict and make improvements on chemical and physical properties of glasses, additional structural information is necessary. This can be obtained through indirect means such as by the measurement of physical properties. The objectives of this program are to obtain structural information by direct and indirect means so that new glasses of improved properties can be made by existing or new techniques.

The main experimental emphasis of this project has been directed towards the measurement of flow and ionic conductivity of oxide glasses as a function of specific volume at various temperatures. Simultaneously theoretical studies were carried out on the calculations of hardness and elastic moduli of glasses. As a result of this two-prong approach equations were derived which permitted the direct calculation of hardness and elastic moduli of numerous oxide glasses. On the experimental side, new glasses with hardness values higher than all known glasses have been prepared. Patent applications are now pending.

Measurements of ionic conductivity and viscous flow under pressure have led to the development of three new techniques to strengthen glasses by chemical ion exchange. Ultra high strength glasses can now be obtained through ion-exchange in significantly shorter times than those which are currently necessary. Patent applications are also pending.

Program Manager: R. W. Haffner, Lt Colonel

COMPLETED PROJECT SUMMARY

1. TITLE: Fast Kinetic Methods Applicable to Trace Chemical Analysis and Detection
2. PRINCIPAL INVESTIGATOR: Professor Dale W. Margerum &
Professor Harry L. Pardue
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907
3. INCLUSIVE DATES: 1 November 1970 to 30 April 1975
4. GRANT NUMBER: AFOSR-71-1988
5. COSTS AND FY SOURCE: \$49,980 FY 71; \$73,901 FY 72
\$55,002 FY 73; \$56,528 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. Barbara A. Burke
Dr. John C. Cooper
Dr. Richard W. Taylor
Dr. John Vasiliades
7. JUNIOR RESEARCH PERSONNEL: J. A. Bittikofer S. Odre
J. J. Czarnecki W. Osgood
H. T. Gaw G. M. Ridder
J. G. Graves D. H. Sanderson
F. P. Hinz G. F. Smith
R. P. Huffman D. E. Williams
M. J. Milano W. H. Woodruff
T. A. Neubecker
8. PUBLICATIONS:

"Kinetics of the Oxidation of 1,2-Diaminocyclohexanetetraacetatoferrate(II) Ion by Iodine," W. H. Woodruff, D. C. Weatherburn and D. W. Margerum, Inorg. Chem. 10, 2102 (1971).

"A Swept Electron Beam Rapid Scan Spectrophotometer, Some Qualitative Aspects," R. E. Santini, M. J. Milano, H. L. Pardue and D. W. Margerum, Anal. Chem. 44, 826 (1972).

"Simple Analog System for Simultaneous Kinetic Analysis," J. B. Worthington and H. L. Pardue, Anal. Chem. 44, 767 (1972).

"Analysis of Mixtures of Aminopolycarboxylic Acids by Chemical Kinetics. Parts per Billion of Nitrolotriacetic Acid in Water," L. C. Coombs, J. Vasiliades and D. W. Margerum, Anal. Chem. 44, 2325 (1972).

"Computer Controlled Stopped-Flow Studies: Application to Simultaneous Kinetic Analyses," D. Sanderson, J. Bittikofer and H. L. Pardue, Anal. Chem. 44, 1934 (1972).

"Thermochemical Parameters of Aqueous Halogen Radicals," W. H. Woodruff and D. W. Margerum, Inorg. Chem. 12, 962 (1973).

"The Electrophilic Acceleration by Bromine of the Elimination of Bromide Ion from $[\text{Co}^{\text{III}}(\text{EDTA})\text{Br}]^{2-}$," W. H. Woodruff and D. W. Margerum, Inorg. Chem. **12**, 958 (1973).

"Kinetics and Mechanism of the Oxidation of Cobalt(II) Aminopolycarboxylate Complexes by Hypobromous Acid and Hypobromite Ion," W. H. Woodruff, D. W. Margerum, M. J. Milano, H. L. Pardue and R. E. Santini, Inorg. Chem. **12**, 1490 (1973).

"Rapid Scanning Spectroscopy: Prelude to a New Era in Analytical Spectroscopy: Prelude to a New Era in Analytical Spectroscopy," R. E. Santini, M. J. Milano and H. L. Pardue, Anal. Chem. **45**, 915A (1973).

"Design and Evaluation of a Vidicon Scanning Spectrometer for Molecular Absorption and Atomic Emission Spectroscopy," M. J. Milano, H. L. Pardue, T. Cook, R. E. Santini, D. W. Margerum and J. M. T. Raycheba, Anal. Chem. **46**, 374 (1974).

"Kinetics of Oxidation of Cobalt(II) Complexes of Ethylenediaminetetraacetate and Cyclohexanediaminetetraacetate by Halogens," W. H. Woodruff, B. A. Burke and D. W. Margerum, Inorg. Chem. **13**, 2573 (1974).

"The Oxidation of Aminopolycarboxylate Complexes of Bivalent Transition Metals by Halogens: Mechanism and Free Energy Relationships," W. H. Woodruff and D. W. Margerum, Inorg. Chem. **13**, 2578 (1974).

"Evaluation of a Vidicon Scanning Spectrometer for Ultraviolet Molecular Absorption Spectroscopy," M. J. Milano and H. L. Pardue, Anal. Chem. **47**, 25 (1975).

"Simultaneous Kinetic Analysis," G. M. Ridder and D. W. Margerum, in press.

"Kinetics of Cyanide Ion Attack on the 1,2-trans-Cyclohexanedinitrilo-N, N, N, N-tetraacetatonickelate(II) Complex," D. C. Young, J. Vasiliades and D. W. Margerum. (in preparation)

"Computer Controlled Instrumentation for Stopped-Flow Studies," H. L. Pardue, L. G. Hargis, R. W. Taylor, and H. Gaw. (in preparation)

"Error Analysis for Two Point Kinetic Analyses," H. L. Pardue and R. W. Taylor. (in preparation)

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main areas of research in this project have concerned the improved detection of chemical species in stopped-flow spectroscopy and the application of kinetic methods to chemical analyses. The research has included: Development of Rapid Scanning Spectrometers using Vidicon Tubes, Development of Computer-Controlled Stopped-Flow Studies, Kinetic Methods of Analysis, Kinetics of Oxidation of Aminopolycarboxylate Complexes of Bivalent Metal Ions by Halogens, and the Detection of Chloramines and the Chemistry of Chloramines.

The development of the rapid scanning spectrometer included the adapting of the spectrometer to an on-line computer, evaluation of the characteristics of vidicon detectors, and application to molecular and atomic spectroscopy. This research area represented the first account of the

quantitative behavior of a vidicon tube over any significant dynamic range and illustrated qualitatively the application to reactions involving intermediates. The results demonstrated applications of the computer interfaced vidicon spectrometer for quantitative studies of fast reactions involving short lived intermediates, as well as demonstrating a linear dynamic range of four orders of magnitude for the silicon target vidicon, including applications to simultaneous multi-element determinations. The capabilities of the vidicon spectrometer were extended into the ultraviolet region and included a study of the source of error in the system.

The development of a completely automated and computer controlled instrumental analytical system included a hierarchical arrangement of a minicomputer and a microcomputer in which the minicomputer sets up the system protocol and handles data acquisition, processing, and display, while the microcomputer controls reagent preparation and stopped-flow mixing functions.

The kinetic methods area included the development of instrumental, computer, statistical, and chemical methods for simultaneous kinetic analysis. Accomplishments in this area included the development of chemical methods for the simultaneous analysis of mixtures of aminopolycarboxylic acids and for trace detection of NTA. Chemical methods were also developed for the simultaneous analysis of mixtures of zinc, cadmium, mercury and copper using zincon. Results were obtained for simultaneous determination of metal ions on an inexpensive analog system capable of processing data graphically from two component first-order reactions.

In the kinetics of oxidation study of aminopolycarboxylate complexes of bivalent metal ions by halogens, the mechanisms of oxidation of $M^{II}L^{2-}$ to the M^{III} complexes by X_2 and X_3^- were studied where M is Fe, Co, and Mn, and L is EDTA and CyDTA. In addition, the rate constants for the reactions of HOBr and OBr^- were determined for the Co^{II} complexes. Some of the main conclusions from this work are as follows:

1. Self-exchange electron-transfer rate constants are calculated to be $8.5 \times 10^4 M^{-1} sec^{-1}$ for I_2 , I_2^- and $29 M^{-1} sec^{-1}$ for Br_2 , Br_2^- . These values are the first to be obtained for self-exchange reactions of the halogens and can be used to predict rate constants for other redox reactions of these halogens. The values are unexpectedly small.
2. The rate constants for the halogens with $Fe^{II}L$ are 9-11 orders of magnitude greater than those of the analogous Mn^{II} and Co^{II} reactions. Nevertheless a general mechanism is proposed in which a one-electron reduction of the halogens takes place after inner-sphere coordination. The activation parameters indicate that the position of the rate-determining step differs with the reactant pairs examined.
3. The rate constants for the reactions of Br_3^- , Br_2 , HOBr and OBr^- with $Co^{II}L^{2-}$ complexes show greatly enhanced reactivity for hypobromous acid and hypobromite ion. An inner-sphere mechanism is proposed where the coordinating ability of OBr^- is important. The OBr^- rate constant is about 2.5×10^4 times larger than the Br_2 rate constant.
4. Steric compression effects of the cyclohexane ring explain the relative rate behavior of the CyDTA complexes compared to the EDTA complexes.

5. Thermodynamic parameters and redox potentials are calculated for $I_2^-(aq)$, $I\cdot(aq)$, $Br_2^-(aq)$ and $Br\cdot(aq)$.

Detection of Chloramines and the Chemistry of Chloramines occupies a practical area of research in that the chlorination of water supplies leads to the formation of chloramines such as NH_2Cl , $NHCl_2$, NCl_3 and $ClNHCHRCOOH$. These compounds are toxic and analytical detection of these species at the parts per billion level is needed. However, there is insufficient knowledge of the chemistry of the interconversion of one chloramine species to another, the chemical reactivity, and the stability of chloramines. The UV rapid scan spectrometer (vidicon) and stopped-flow experiments have been used to characterize some of the chemical behavior of the chloramines at millimolar concentration levels. This work has led to the first determination of the protonation constant of monochloramine, $\log K_H = 1.4$. Preliminary studies have concerned the kinetics of formation of NH_2Cl from NH_3 and the kinetics of its interconversion reactions to $NHCl_2$ and NCl_3 in more acidic solutions.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Quantum Theoretical Studies of Gas-Solid Interactions.
2. PRINCIPAL INVESTIGATOR: Drs. Richard P. Messmer and
Charles W. Tucker, Jr.
General Electric Company
Physical Chemistry Laboratory
Schenectady, New York
3. INCLUSIVE DATES: 1 September 1971 - 30 June 1975
4. CONTRACT NUMBER: F44620-72-C-0008
5. COSTS AND FISCAL RESOURCE: \$32,000 FY-72; \$2,125 FY-73; \$25,000 FY-74;
\$30,000 FY75
6. SENIOR RESEARCH PERSONNEL: None.
7. JUNIOR RESEARCH PERSONNEL: None.
8. PUBLICATIONS:

"A Molecular Orbital Approach to Chemisorption III. Atomic H and O on Graphitic BN". B. McCarroll and R. P. Messmer, Surface Sci. 27, 451 (1971).

"A Molecular Orbital Approach to Chemisorption IV. LCAO Band Structures and the Molecular Unit Cell". R. P. Messmer, B. McCarroll and C. M. Singal, J. Vac. Sci. Tech. 9, 891 (1972).

"Orbital Symmetry Rules for Chemisorption and Catalysis". R. P. Messmer and A. J. Bennett, Phys. Rev. B6, 633 (1972).

"Localized Electronic Excitations in Transition-Metal Oxides". K. H. Johnson, R. P. Messmer and J. N. D. Connolly, Solid State Commun. 12, 313 (1973).

"A Theoretical Interpretation of Electron Energy Spectra for Oxygen Chemisorbed on Ni". R. P. Messmer, C. W. Tucker, Jr., and K. H. Johnson, Surface Sci. 42, 341 (1974).

"Clusters, Chemisorption and Catalysis". K. H. Johnson and R. P. Messmer, J. Vac. Sci. Tech. 11, 236 (1974).

"Theoretical Studies of Metal Aggregates and Organo-Metallic Complexes Relevant to Catalysis". R. P. Messmer, Proceedings of the Battelle Colloquium on "The Physical Basis of Heterogeneous Catalysis", Gstaad, Switzerland. Plenum Press (New York, 1975) in press.

"A Comparison of the SCF-Xa-SW and Extended Huckel Methods for Metal Clusters". R. P. Messmer, C. W. Tucker and K. H. Johnson, submitted for publication.

"The Molecular Cluster Approach to Some Solid State Problems", R. P. Messmer in "Modern Theoretical Chemistry" Vol. 4. edited by G. A. Segal, Plenum Press, to be published.
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the research was to obtain basic understanding regarding the nature of gas-solid interactions -- which are of fundamental importance in chemisorption, catalysis and other surface phenomena -- by performing quantum mechanical calculations on model systems. Because of the complexity of the

problem, one of the important contributions of this research was simply the investigation of various quantum mechanical methods and models of a surface in order to obtain appropriate methods and models which were computationally feasible, yet accurate enough to be physically meaningful. Although Molecular Orbital Methods were investigated at three levels of sophistication and models of the surface were used which involve both clusters of atoms and semi-infinite slabs, one thing became clear at the outset of the work. That is, traditional Hartree-Fock (HF) ab initio methods are at present computationally far too demanding to be able to treat a physically interesting system. The AFOSR supported program investigated the efficiency of the following three methods: (1) the extended Huckel (EH) method, (2) the CNDO method and (3) the self consistent field X-Alpha scattered wave method (SCF-Xa-SW). We used the CNDO and EH methods to investigate chemisorption of simply atoms such as H, O, and on clusters of graphitic BN and on a slab of graphite. From these studies as well as from a number of unpublished calculations, it was learned that (1) the EH method can provide a useful description of certain aspects of chemisorption on non-transition metals if the charge transfer between any two atoms in the system is rather small (i.e., $\leq .2e$), (2) for greater charge transfer, a self consistent method is essential and for systems composed of first and second row atoms, the CNDO method can provide useful information, (3) for transitional-metal substrates, EH and CNDO are not reliable, only the SCF-Xa-SW method can be used.

AFOSR Program Manager: R. W. Haffner, Lt Col.

COMPLETED PROJECT SUMMARY

1. TITLE: Influence of Collision Cross-Sections for Electrons, Atoms and Molecular Systems
2. PRINCIPAL INVESTIGATOR: Dr. H. H. Michels
United Technologies Research Center
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 1 April 1971 to 31 March 1975
4. CONTRACT NUMBER: F44620-71-0066
5. COSTS AND FY SOURCE: \$36,235 FY 71; \$35,846 FY 72; \$18,902 FY 73
\$32,182 FY 74; \$25,455 FY 75
6. RESEARCH PERSONNEL: Dr. H. H. Michels
7. PUBLICATIONS:

"Calculation of the Integrated Band Intensities of NO," H. H. Michels, J. of Quant. Spectr. and Radiat. Transf. 11, 1735 (1971).

"The Deactivation of the Asymmetric Stretch Mode of Carbon Dioxide by Hydrogen," H. J. Kolker, Chem. Phys. Ltrs. 10, 498 (1971).

"Ab Initio Calculation of the $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ Oscillator Strengths in AlO," H. H. Michels, J. of Chem. Phys. 56, 665 (1972).

"Variational Approach to the Quantum Theory of Scattering II. The Kohn Method and Kato Eigenvalue Problem," H. J. Kolker, J. of Chem. Phys. 58, 2288-2297 (1973).

"A Variational Approach to the Quantum Theory of Scattering III. The Expansion Techniques of Harris and Michels," H. J. Kolker, submitted for publication in The Journal of Chemical Physics.

"Configuration Interaction Studies of the HeH^+ Molecular Ion. I Singlet Sigma States," T. A. Green, H. H. Michels, J. C. Browne, and M. M. Madsen, J. of Chem. Phys. 61, 5186 (1974).

"Analysis of Dipole-Allowed Electronic Transitions in Diatomic Molecules," H. H. Michels, Energy, Structure, and Reactivity, edited by Darwin W. Smith and Walter B. McRae, John Wiley and Sons, Inc., 1973.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research performed under this contract was directed toward the analysis of collisional processes involving electrons, ions and molecules. Collisional processes have long been recognized as being of substantial interest in basic physical processes, as well as in a number of engineering applications, particularly in the fields of propulsion and power generation. The amount of experimental data is limited and difficulties are encountered in making exact measurements at low energies. Therefore, a theoretical

approach to predict kinetic cross-sections appeared necessary. The development of practical approaches and their implementation through the construction of efficient computer programs for predicting kinetic cross-sections comprise the goals of this research program. Research was performed in the areas of electron-atom, electron-molecule, atom-atom, and molecule-molecule collisions.

A computer code has been developed for predicting the elastic and inelastic cross sections for electron-atom collisions in the energy range-zero to near threshold. This code is based on a non-arbitrary variational formulation for expansion-type scattering which indicate accuracies comparable to the best ever obtained, but with total computation times of only seconds.

Research in heavy particle collision theory was directed toward practical solutions of the coupled differential equations describing scattering for resonant or near-resonant processes in the thermal energy region. Studies were also carried out on the analysis and classification of adiabatic and non-adiabatic descriptions of low-energy collisions. The system $\text{Li} + \text{Li}^+$ was examined in detail for diabatic collision paths. In addition, some studies of collisional excitation of molecules by electron impact were initiated. A study of the temperature dependence of dissociative-recombination kinetics in nitrogen was performed.

A new method has been developed for calculating upper and lower bounds on the energies of resonance and Ramsauer-Townsend states. This method is based on the theory that the Kohn variational technique for solving scattering problems is equivalent to a variational method for calculating a special set of eigenfunctions in terms of which the solution to the scattering problem is expanded.

Studies were undertaken of the theory for dipole-allowed transitions in diatomic molecules. A consistent nomenclature was derived. Intensity factors such as f-numbers, Einstein coefficients and band strengths were all developed in an interrelated form.

A procedure was developed for evaluating bound-free elements by making use of the observation that an electron incident on a molecular ion can be regarded as an ionized Rydberg state of the molecule, AB.

A new method has been developed for transformation of a basis set of one-electron Slater orbitals to an orthogonal framework which resembles most closely the original non-orthogonal atomic set. This new method is basically a modification of a transformation suggested by Löwdin some years ago.

New computational methods based on the free-electron exchange approximation ψ_a have been developed during the past year and extended ab initio procedures have been studied for constructing potential energy surfaces. The new method under study is based on the scattered wave formalism which has been applied in the past to solid state calculations. The two basic differences between this approach and an ab initio approach are: 1) the use of a localized exchange potential, thus eliminating the problem of multi-center integrals and 2) the use of a muffin-tin or constant potential between spheres of charge centrally located on the atomic nuclei.

Other activities included extensive modification of the Research Center's CI polyatomic programs.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Calculations of Electronic Wave Functions
2. PRINCIPAL INVESTIGATOR: Dr. H. H. Michels
United Technologies Research Center
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 1 June 1974 to 31 May 1975
4. CONTRACT NUMBER: F44620-74-C-0083
5. COST AND FY SOURCE: \$44,882 FY 74
6. RESEARCH PERSONNEL: Dr. H. H. Michels
7. PUBLICATIONS:

"Calculation of Electronic Wave Functions," H. H. Michels, Final Report, Aug 1975.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The release of certain chemical species into the upper atmosphere results in luminous clouds that display the resonance electronic-vibrational-rotation spectrum of the released species. Such spectra are seen in rocket releases of chemicals for upper atmospheric studies and upon reentry into the atmosphere of artificial satellites and missiles. Of particular interest in this connection is the observed spectra of certain metallic oxides. From band intensity distribution of the spectra, and knowledge of the f-values for electronic and vibrational transitions, the local conditions of the atmosphere can be determined.

Present theoretical efforts which are directed toward a more complete and realistic analysis of the transport equations governing atmospheric relaxation and the propagation of artificial disturbances require detailed information of thermal opacities and LWIR absorption in regions of temperature and pressure where molecular effects are important. Because of inherent difficulties in the experimental determination of such properties, a theoretical program for calculating band absorption and emission coefficients was initiated. This theoretical program is based on current quantum mechanical techniques and capabilities for determining electronic and vibrational transition probabilities.

Calculations have been performed for band-to-band transition probabilities. The systems under study were NiO, ThO, ThO⁺, CuO and CrO. Electronic wavefunctions have been constructed for selected states of these molecules and expectation values of the electronic energy and electric dipole transition moments have been calculated. The calculated electric dipole transition moments were combined with accurate numerical vibrational-rotational wavefunctions, based on RKR potential functions, to yield estimates of the system f-numbers. Data are presented for the transitions (³Π - ³Σ⁻) of NiO, (³Π - ³Σ⁺) of CrO and (A¹Σ⁺ - X¹Σ⁺) of ThO.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Electronic and Magnetic Properties of High Temperature Electrolytes
2. PRINCIPAL INVESTIGATOR: Professor Norman H. Nachtrieb
Department of Chemistry
The University of Chicago
5801 Ellis Ave
Chicago, Illinois 60637
3. INCLUSIVE DATES: 1 September 1970 to 31 August 1974
4. GRANT NUMBER: AFOSR-71-1962
5. COSTS AND FY SOURCE: \$24,000 FY 70; \$17,636 FY 71; \$40,676 FY 72
\$56,721 FY 73; \$44,892 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. Chen Hsu
7. JUNIOR RESEARCH PERSONNEL: Mitchel Sosis
8. PUBLICATIONS:

"Advances in Chemical Physics," I. Prigogine, S. A. Rice and N. H. Nachtrieb, Vol. 31, p. 465, John Wiley & Son, 1975.

"Electrical Conductance of Cs-bl," Chen Hsu and N. H. Nachtrieb, in preparation.

"Electrical Conductance of Rb-RbCl," Chen Hsu and N. H. Nachtrieb, in preparation.

"The Design of an Electrical Conductance Cell," Chen Hsu and N. H. Nachtrieb, in preparation.

"The Excess Free Energy of Solution of Cs and Rb in Their Molten Chlorides," Chen Hsu and N. H. Nachtrieb, in preparation.

"The ESR of Na-NaCl Molten Solutions," M. Sosis and N. H. Nachtrieb, submitted to J. Chem. Phys.

"Electronic and Magnetic Properties of High Temperature Electrolytes," N. H. Nachtrieb, Final Scientific Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

These studies of high temperature molten electrolytes have the objective of understanding the nature of the electron in the solutions that result when an alkali metal is dissolved in an alkali metal halide. The properties of such solutions are intermediate between those of pure molten salts, on the one hand, and of pure liquid metals, on the other. Superimposed upon the electrolytic transport properties due to cations and anions is the contribution made by electrons. This contribution does not appear to be a simple, additive one, and it is the goal to delineate the nature of the interaction between the mobile electron

with positive and negative ions and the manner in which this interaction varies with temperature and the concentration of dissolved metal.

Although the focus of this research is upon the alkali metals and their halide salts, it is a problem with much broader implications. Mixed ionic/electronic molten electrolytes include the alkaline earth and rare earth metals in their corresponding halide salts, as well as copper in cuprous sulfide. In fact, numerous metals have a small but finite solubility in their molten chalcogenides, a fact which has relevance for their high temperature corrosive failure.

The purpose of understanding the electron-ion plasma electrolytes, which are formed when an alkali metal is dissolved in a molten alkali halide having a common cation, has been considerably advanced through the studies of the electrical conductance, the magnetic susceptibility, the electron spin resonance, and the freezing point lowering of these metal-metal halide electrolytes.

The significant conclusions are:

1. At low dissolved metal concentrations the valence electron of the solute metal is locally trapped in a cage of its nearest-neighbor anions, in a state that closely resembles that of the F-center in the corresponding additively colored crystalline alkali halide.
2. The electrolytes are semiconductors at low to moderate dissolved metal concentrations. The electronic and ionic contributions to the electrical conductance are equal at approximately 1 mole percent dissolved metal; above this concentration the electrical conductance is dominated by a thermally activated electron hopping mechanism.
3. The non-metal-to-metal transition is broad, occurring at 40 mole percent cesium in the Cs-CsCl system and at 20 mole percent rubidium in the Rb-RbCl system.
4. Analysis of freezing point depression data for the Cs-CsCl and Rb-RbCl systems reveals large positive excess free energies of solution ($5 - 6 \text{ k.cal.mole}^{-1}$), verifying the predictions of Pitzer's F-center model.
5. Electron spin resonance of the valence electron of the dissolved metal was observed in the molten Na-NaCl system. The electronic g value shows a dramatic decrease with dissolved metal concentration, which is qualitatively interpreted in terms of the transition from the localized F-center-like state to extended states of the electron.
6. Magnetic susceptibility measurements reveal the existence of nondegenerate localized states of the electron at low dissolved metal concentration, with increasing spin-paring as the metal concentration is increased.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Properties of Rotaxane Compounds

2. PRINCIPAL INVESTIGATOR: Dr. Melvin S. Newman
Department of Chemistry
Ohio State University
Research Foundation
Columbus, Ohio 43212

3. INCLUSIVE DATES: 1 February 1972 to 30 September 1974

4. GRANT NUMBER: AFOSR-72-2237

5. COSTS AND FY SOURCE: \$43,600 FY 72; \$20,205 FY 74

6. SENIOR RESEARCH PERSONNEL: Dr. S. Gromalski
Dr. V. Khanna
Dr. R. Robey

7. JUNIOR RESEARCH PERSONNEL: L. F. Lee

8. PUBLICATIONS:

"The Synthesis of Arylacetylenes. 3,5 Di-tert-butylphenylacetylene,"
Melvin S. Newman and Len Fang Lee, J. Org. Chem. 37, 4468 (1972).

"High Dilution Cyclization of Polyoxapentacosanodinitriles,"
submitted to J. Org. Chem.

"Synthesis and Properties of Rotaxane Compounds," Melvin S. Newman,
Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to prepare rotaxane compounds by an improved procedure and to study their physical and chemical properties. Rotaxanes are unique in that two different molecules are held together by interlocking but not by a chemical bond.

Although several intermediates were prepared successfully, all attempts to prepare rotaxane compounds through coupling reactions failed to yield appreciable amounts of the desired rotaxanes.

A new synthesis of benz[a]pyrene derivatives was worked out. This work is being written up for publication. Also, a paper entitled, "High Dilution Cyclization of Polyoxapentacosanodinitriles has been submitted for publication in the Journal of Organic Chemistry.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemical Studies in Aluminum Chloride Melts
2. PRINCIPAL INVESTIGATOR: Professor Robert A. Osteryoung
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523
3. INCLUSIVE DATES: 1 January 1971 to 28 February 1975
4. GRANT NUMBER: AFOSR-71-1995
5. COSTS AND FY SOURCE: \$38,079 FY 71; \$39,486 FY 72
\$35,036 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. Roger Abel
Dr. Larry Boxall
Dr. Robert Gale
Dr. H. L. Jones
Dr. Raouf Loutfy
Dr. Jane Osteryoung
7. JUNIOR RESEARCH PERSONNEL: Kenneth Drake
Dr. H. E. Keller
Dr. B. H. Vassos
8. PUBLICATIONS:

"The Advantage of Charge Measurements for Determining Kinetic Parameters," Janet Osteryoung and R. A. Osteryoung, Electrochimica Acta **16**, 525 (1971).

"Introduction to the On-Line Use of Computers in Electrochemistry," Vol II, R. A. Osteryoung, "Application of Computers to Chemical Instrumentation," Ed. by Mattson, Mark, and MacDonald, MARCEL DEKKER (1973).

"Solvent Equilibria in AlCl_3 -NaCl Melts," L. G. Boxall, H. L. Jones and R. A. Osteryoung, J. Electrochem. Soc. **120** (2), 223 (1973).

"Organic Electrode Reactions in Fused AlCl_3 Containing Solvents," H. Lloyd Jones, L. G. Boxall and R. A. Osteryoung, J. Electroanalytical Chem. **38**, 476 (1972).

"Electrochemical Studies on Ag, Fe and Cu Species in AlCl_3 -NaCl Melts," L. G. Boxall, H. L. Jones and R. A. Osteryoung, J. Electrochem. Soc. **121**, 212 (1974).

"Electrode Reactions of Aromatic Amines in Solvents Containing Fused AlCl_3 , II.," H. Lloyd Jones and R. A. Osteryoung, J. Electroanalytical Chemistry **49**, 281 (1974).

"Investigation of Subvalent Ion Effects During Aluminum Anodization in Molten NaCl- AlCl_3 Solvents," R. J. Gale and R. A. Osteryoung, J. Electrochem. Soc. **121**, 983 (1974).

"Reductive Defunctionalization of 1-substituted Adamantanes in Molten Sodium Tetrachloroaluminate," V. R. Koch, L. L. Miller, and R. A. Osteryoung, J. Organic Chemistry, **39**, 2416 (1974).

"Organic Reactions in Molten Tetrachloroaluminate Solvents," H. Lloyd Jones and R. A. Osteryoung, in press, "Advances in Molten Salt Chemistry," Vol. 3, Ed. by J. Braunstein, G. P. Smith and G. Mamantov, Plenum Press, (1975).

"Dissociative Chlorination of Nitrogen Oxides and Oxyanions in Molten Sodium Chloride-Aluminum Chloride Solvents," R. J. Gale and R. A. Osteryoung, Inorganic Chem. **14**, 1232 (1975).

"An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt," H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, J. Am. Chem. Soc. **97**, 3264 (1975).

"The Electrochemical Oxidation of N,N,N',N'-Tetramethylbenzidine in Molten Sodium Tetrachloroaluminate," D. E. Bartak and R. A. Osteryoung, J. Electrochem. Soc. **122**, 600 (1975).

"The Electrochemical Behavior of Quinones in AlCl_3 -NaCl Fused Salt Solvents; Rotating Disc Electrode Studies," D. Bartak and R. A. Osteryoung, (accepted Electroanal. Chem)

"Fabricating a Ring-Disc Electrode for Molten Salt Studies," J. Phillips, R. Gale and R. A. Osteryoung, submitted to Anal. Chem.

"Electrochemical Study of Sulfur in AlCl_3 -NaCl Fused Salt Solvents," K. A. Paulsen and R. A. Osteryoung, submitted to J. Electrochem. Soc.

"Solubilization of Metal Sulfides by AlCl_3 --Solvent Systems," K. A. Paulsen and R. A. Osteryoung.

"Electrochemical Studies of Mo-Species in AlCl_3 -NaCl Molten Salt Solvent," J. Phillips and R. A. Osteryoung.

"Electrochemical Oxidation of Hexamethylbenzene in a Room Temperature AlCl_3 --Molten Salt Solvent, V. R. Koch, L. L. Miller and R. A. Osteryoung, submitted to JACS. Final Report "Electrochemical Studies in Aluminum Chloride Melts"

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Fundamental electrochemical studies of a variety of solute species, both inorganic and organic, have been carried out in aluminum halide based melts, mainly the AlCl_3 :NaCl (1:1) system, but also in the room temperature melt, ethylpyridinium bromide - AlCl_3 (1:2). Chemical equilibrium measurements have been made to determine the solvent equilibrium in the AlCl_3 -NaCl system. Several metal ions - species of Fe, Cu and Ag - have been studied in the melt as well as a number of organic amines. The oxidation of tetramethylbenzidine has been studied in detail and a mechanism developed. The electrochemical behavior of benzoquinone and tetrachloroquinone has been studied employing chronoamperometric, pulsed voltammetric, cyclic voltammetric, rotating disc and coulometric techniques.

Studies of nitrogen oxides, sulfur and molybdenum oxides have been carried

out in the AlCl_3 - NaCl system. The NO-NO^+ couple has been found to have very fast, reversible kinetics. Sulfur is quantitatively reduced to sulfide in both the basic and acid melts; a number of metal sulfides have been found to be quite soluble in the acid melts. Sulfur appears to be oxidized to S_2Cl_2 , and to other, as yet unknown, species. The oxides and oxychlorides of molybdenum are electroactive, but very complex in behavior. Mo(VI) is reduced to Mo(III) ; additional electrochemistry has not yet been sorted out. Use has been made of the first ring-disc electrode fabricated for molten salt work in these studies.

The oxidation of hexamethylbenzene has been studied in the room-temperature melt and the products identified as penta- (or tetra) methylbenzene and diphenylmethane. The behavior of two iron-diimine complexes has also been studied in this melt.

An important part of the study was a procedure for melt purification. Initial melt preparations are usually light straw colored, and prolonged pre-electrolysis between two aluminum electrodes results in removal of all color and a water-like, absolutely clear solution. Since all the experimental work was carried out in Vacuum Atmospheres dry boxes, the standard procedure followed was to prepare large batches of molten NaAlCl_4 and pipet aliquots into the cells used for detailed experimentation.

There was an interest in exploring the behavior of a number of metal ions. Cu, Ag, and Fe were studied by a variety of techniques; cyclic voltammetry, potentiometry, and normal pulse voltammetry (7). Fe was of particular interest, because it had been felt that the straw color of the impure melt was due to iron. Silver was of interest because it was desirable to find a metal/metal ion couple independent of pCl^- to use as a reference. Cu was chosen because the guess was that the (I) and (II) states might show different pCl^- dependencies. The resultant work indicated that Fe electrochemistry is very straight forward; Fe(III) is reduced to Fe(II) and then to the metal. Within the scope of the quantitative methodology employed - pulse voltammetry - the electrode processes appear reversible. The Ag/Ag(I) couple had only a slight change in standard potential - from 1.086 to 1.106 on changing from the 1:1 to the 2:1 melt which indicates little effect of the formation of chloro complexes. Cu, on the other hand, formed CuCl_2 , as deduced from E.M.F. - $[\text{Cu}^+]$ plots, and the equilibrium constant was determined by appropriate curve fitting. E^0 values for $\text{Cu}^{++} - \text{Cu}^+$ and $\text{Cu}^+ - \text{Cu}$ were determined.

Both FeCl_2 and CuCl had limited solubility in the basic melt. It was almost impossible to anodize Fe [to form Fe(II)] into the melt in the basic system. When the melts were acidified (AlCl_3 - NaCl), these solubility problems disappeared. In summary, the electrode processes for the pertinent Ag, Cu, and Fe couples were reasonably "well behaved."

Since a good deal of the AlCl_3 melt literature remarks on the "pale yellow" melt coloration, and since it was found that apparently high melt purity can be attained by pre-electrolysis and can be maintained in a good dry-box atmosphere, it was sought to obtain evidence for Al(I) existing in the melt. A number of low-valent entities have been identified in these melts at high acidities and the question of Al(I) seemed to be less than settled. Prolonged pre-electrolysis between two aluminum electrodes resulted in a "dark" deposit forming in the cathode. Analysis of the deposit by emission spectrography after extraction of the adherent salt with liquid SO_2 (13) indicated the major metallic constituents to be Bi, Sn, Mn, and Al. Once this "dark" deposit formed, no further deposit formed on a fresh Al

surface after melts had been purified by sufficient periods of pre-electrolysis. Electrodeposition and stripping were carried out at constant current at both tungsten and vitreous carbon electrodes. The efficiency of the plating/stripping process was found to be 100% in terms of Al(III) reduction to the metal and oxidation back to the +3 state. In the range of apparent current densities $0.03\text{--}6.30\text{ mA cm}^{-2}$, in both the 1:1 and 2:1 molar $\text{AlCl}_3\text{--NaCl}$ systems, no deviation from a faradaic three electron yield could be established. If the electrode were "open circuited" between deposition of Al(0) and its stripping, then a small corrosion process was detected, in both acid and basic melts, which corresponded to a loss of 9×10^{-12} moles Al/cm²/sec, compared to a value at least 10^3 higher quoted elsewhere. Thus, it was concluded that reports of Al(I), at least in the $\text{AlCl}_3\text{--NaCl}$ system in the 175°C range, are due to impurities; that is, electroactive substances tend to oxidize Al(0), which gives an apparent anodic current efficiency greater than predicted.

An increased interest in studies of oxygenated entities which might have potentialities as battery cathodes in NaCl--AlCl_3 systems encouraged the group to return to the study of N-O work. To do this, it was decided to attempt to fabricate a high-temperature ring disc electrode. While they had previously utilized a rotating-disc electrode system, sealing vitreous carbon into pyrex by an established procedure, no ring-disc electrode had been made.

The ring disc electrode employs glassy carbon G.C. 30 pipe (6 mm internal diameter) and glassy carbon G.C. 30 rod (3 mm diam.), obtained from Tokai Electrode Mfg. Ltd. The electrode consists of an 8 mm glassy carbon disc with an annular ca. 1 mm glass separator and an approximately 2 mm wide disc. Detection at the ring of electroactive intermediate species formed at the disc depends on the "transit time" - the time required for the hydrodynamic transport of material from the disc across the glass space to the ring. The "transit time" in the $\text{AlCl}_3\text{--NaCl}$ system is also increased by the greater viscosity, and attendant smaller diffusion coefficients found in this melt. Nevertheless, calculations indicate that at 10,000 r.p.m. one would be able to detect an electroactive intermediate, produced at the disc and decaying by first or pseudo-first order kinetics, with a half-life of the order of 10 msec. It is felt, that one can operate at rotation rates considerably in excess of 10,000 r.p.m., which is the maximum value for the current rotator. Hence, halflives less than 10 msec may be attainable.

The present electrode, however, is eminently satisfactory in that it permits a technique of great flexibility and utility to be successfully employed under very stringent experimental conditions in molten salts.

The electrodes thus far fabricated have only been employed in solvents at up to 200°C. However, since they are heated to above 900°C during fabrication, it is conceivable that they may also be useful in higher temperature systems, such as KCl--LiCl ; the coefficients of thermal expansion of pyrex and vitreous carbon are sufficiently different to suspect that some leakage may occur at higher temperatures. However, the nature of the electrode construction and possible wetting of the carbon by the glass may act in concert to permit operation in excess of 200°C.

This Group has also demonstrated the first reasonable electrochemical synthesis in a molten salt system. In a mixture of 2:1 aluminum chloride:ethylpyridinium bromide melt and benzene (~1:1 volume melt: benzene) hexamethylbenzene can be anodically oxidized at either tungsten

or vitreous carbon electrodes to pentamethylbenzene and diphenylmethane. The synthetic scope of this Friedel-Crafts like reaction in which product and current yields approach 100% is potential dependent, i.e., the reaction can be set at a potential to yield pentamethyl - or tetramethylbenzene and diphenylmethane. In short, hexamethylbenzene can be selectively and quantitatively demethylated to mesitylene and diphenylmethane. Clearly, the chemical nature of the molten salt medium itself determines the kinds of products obtained as well as their relative distribution after the initial electron transfers.

The mechanism of this surprisingly clean and quantitative electrode reaction is currently being studied, utilizing a variety of electrochemical methods, including the ring-disc technique.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Gas Phase Reactions of Atoms, Ions and Simple Molecules
Related to Upper Atmosphere Chemistry
2. PRINCIPAL INVESTIGATOR: Professor Leon F. Phillips
Chemistry Department
University of Canterbury
Christchurch, NEW ZEALAND
3. INCLUSIVE DATES: 1 May 1971 to 30 April 1975
4. GRANT NUMBER: AFOSR-71-2134
5. COSTS AND FY SOURCE: \$19,900 FY 71; \$14,000 FY 73
\$8,000 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. S. W. Bennett
Dr. R. F. C. Claridge
Dr. P. J. Domaille
Dr. C. G. Freeman
Dr. R. G. A. R. MacLagan
Dr. E. F. McCoy
Dr. M. J. McEwan
Prof H. I. Schiff
Dr. J. B. Tellinghuisen
Prof C. A. Winkler
7. JUNIOR RESEARCH PERSONNEL: Tan Hee Choo
Gavin J. Dougherty
Michael R. Dunn
Ong Kean Ghee
Ron L. Griffiths
Donald R. Hastie
Gerard P. Horgan
Alan G. Ladd
John P. Liddy
Peter D. Morten
Juliet N. Mulvihill
Herman J. Vreede
8. PUBLICATIONS:

"Photometric and Mass Spectrometric Observations on the Reaction
of Hydrogen Atoms with Cyanogen," M. R. Dunn, C. G. Freeman,
M. J. McEwan and L. F. Phillips, J. Phys. Chem. 75, 2662 (1971).

"LiO Formation in dry Carbon Monoxide Flames," G. J. Dougherty,
M. R. Dunn, M. J. McEwan and L. F. Phillips, Chem. Phys. Letrs. 11,
124 (1971).

"Quantum Yields in the 58.4 nm Photolysis of CO₂," J. B. Tellinghuisen,
C. A. Winkler, S. W. Bennett and L. F. Phillips, J. Phys. Chem. 75,
3499 (1971).

"Phase-Shift Studies of Hg(³P₀) Reactions. Part 3. Complexes of
Hg(³P₀) With Some Primary Amines," C. G. Freeman, M. J. McEwan,

R. F. C. Claridge and L. F. Phillips, Trans Faraday Soc. 67, 3247 (1971).

"Band Fluorescence of Xenon," C. G. Freeman, M. J. McEwan, R. F. C. Claridge and L. F. Phillips, Chem. Phys. Letrs. 10, 530 (1971).

"I. General Design Considerations; III. Basic Electrical Principles; IV. Electronic Components; VI. Detection (Transducers)," L. F. Phillips in Physical Methods of Chemistry, Eds. A. Weissberger and B. W. Rossiter, Interscience (New York) 1971.

"Mass Spectrometric Observations on the Reaction of Hydrogen Atoms with ICN," G. P. Horgan, M. R. Dunn, C. G. Freeman, M. J. McEwan and L. F. Phillips, J. Phys. Chem. 76, 1392 (1972).

"Quantum Yields in the 58.4 nm Photolyses of NH_3 and H_2O ," J. B. Tellinghuisen, C. A. Winkler and L. F. Phillips, J. Phys. Chem. 76 298 (1972).

"Quenching rates for CO_2^+ Emission Excited by 58.4 nm Irradiation of CO_2 ," C. A. Winkler, J. B. Tellinghuisen and L. F. Phillips, J. Chem. Soc. Faraday Trans II, 68, 121 (1972).

"Quenching Rates for N_2^+ , N_2O^+ and CO_2^+ Emission Bands Excited by 58.4 nm Irradiation of N_2 , N_2O and CO_2 ," J. B. Tellinghuisen, C. A. Winkler, C. G. Freeman, M. J. McEwan and L. F. Phillips, J. Chem. Soc. Faraday Trans II, 68, 833 (1972).

"Excimer Formation by NH_3 and $\text{Cd}(\text{}^3\text{P}_0)$," P. D. Morten, C. G. Freeman, M. J. McEwan, R. F. C. Claridge and L. F. Phillips, Chem. Phys. Letrs. 16, 148 (1972).

"Some Photometric Observations of Trace Additives in Dry Carbon Monoxide Flames," G. J. Dougherty, M. J. McEwan and L. F. Phillips, Combustion and Flame 21, 253 (1973).

"Phase-Shift Studies of $\text{Hg}(\text{}^3\text{P}_0)$ Reactions. Part 4. Observations of the Hg_2 Emission Bands at 335 nm and 485 nm," A. G. Ladd, C. G. Freeman, M. J. McEwan, R. F. C. Claridge and L. F. Phillips, J. Chem. Soc. Faraday Trans II, 69, 849 (1973).

"Phase-Shift Study of the 147 nm Xenon-Sensitized Fluorescence of CO," C. G. Freeman and L. F. Phillips, Chem. Phys. Letrs. 20, 96 (1973).

"Modulation Techniques in Chemical Kinetics," L. F. Phillips, in Progress in Reaction Kinetics, Eds. K. R. Jennings and R. B. Cundall, Pergamon Press (London), 1973, Vol. 7, p. 83.

"Quenching and Trapping of Lyman- α Fluorescence at Large Optical Depths," L. F. Phillips, Can. J. Chem. 51, 1517 (1973).

"Computer Simulation of Phase-Shift Measurements of the Quenching and Trapping of Resonance Radiation at Large Optical Depths," L. F. Phillips, J. Photochem. 2, 255 (1973).

"Origin of the 550 nm Band of Hg_2 ," L. F. Phillips, Chem. Phys. Letrs. 21, 28 (1973).

"Pollution of the Upper and Lower Atmosphere," L. F. Phillips, in Environment and Industry, N. Z. Institute of Chemistry 1973.

"Revised Rate Constants for Quenching Reactions of Excited CO_2^+ , N_2O^+ and N_2^+ ," C. G. Freeman and L. F. Phillips, Can. J. Chem. **52**, 426 (1974).

"Mercury-Sensitized Luminescence," L. F. Phillips, Accounts of Chem. Research **7**, 135 (1974).

"Phase-Shift Study of the Quenching and Trapping of Cd 228.8 nm Resonance Radiation," P. D. Morten, C. G. Freeman, R. F. C. Claridge and L. F. Phillips, J. Photochem. **3**, 285 (1974).

"Cd, Fluorescence from Low-Temperature Solids," H. J. Vreede, R. F. C. Claridge and L. F. Phillips, Chem. Phys. Letrs. **27**, 1 (1974).

"Molecular Orbital Calculations for Dinitrogen Tetroxide and Related Molecules," R. L. Griffiths, R. G. A. R. MacLagan and L. F. Phillips, Chem. Phys. **3**, 451 (1974).

"Laboratory Measurements of Some Ion-Molecule Reactions Related to Sulphur Chemistry in Interstellar Clouds," J. P. Liddy, C. G. Freeman and M. J. McEwan, Astrophysical Letters, in press, 1975.

"Chemistry of the Atmosphere," M. J. McEwan and L. F. Phillips, Edward Arnold (London), 1975.

"Breakdown of Cyanogen in Fuel-Rich $\text{H}_2/\text{N}_2/\text{O}_2$ Flames," J. N. Mulvihill and L. F. Phillips, 15th Symposium (International) on Combustion, in press.

"Dissociation Energies of Alkali Metal Cyanides," J. N. Mulvihill and L. F. Phillips, Chem. Phys. Letrs., in press.

"Products of the Reaction of NO with NH," J. N. Mulvihill and L. F. Phillips, submitted to Chem. Phys. Letrs.

"Phase-Shift Studies of $\text{Hg}(^3\text{P}_0)$ Reactions. Part 5. Kinetics of Hg_2 Excimers in the Presence of Nitrogen," Ong K. G., C. G. Freeman, M. J. McEwan and L. F. Phillips, J. Chem. Soc. Faraday Trans II, in press.

"Numerical Studies of the Growth and Decay of Resonance Fluorescence in the Presence of Quenching and Radiation Trapping," L. F. Phillips, J. Photochem., in press.

"Gas Phase Reactions of Atoms, Ions and Simple Molecules Related to Upper Atmosphere Chemistry," L. F. Phillips, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Work on atom-molecule and ion-molecule reactions in flow systems has made steady progress. Current work is concerned with radical reactions involving methyl nitrite and related species and with ion-molecule reactions involving species containing sulphur and cyanide. Flame work of Dr. Phillips and his research group

currently emphasizes the detailed comparison of numerical simulation results and experimental findings about breakdown processes in the primary reaction zone of a flame. The reaction of NO with NH which has been studied in the flames is interesting as a possible means of removing NO from engine exhaust gas. Thus it is of great potential importance in relation to the alleviation of photochemical smog and SST pollution of the stratosphere.

Work on 58.4 nm photolyses of small molecules and the fluorescence of excited molecular ions generated during such photolyses came to a natural end at about the same time as the supply of thin (100 nm) aluminium windows ran out. These windows are needed to transmit the helium resonance radiation.

Phase-shift studies of excited atom reactions continue; the $\text{Hg}(^3\text{P}_0)$ work is now concentrated on the emission bands of Hg_2 . Other work involves excited xenon atoms, hydrogen atoms and cadmium atoms. Reviews of the uses of the phase-shift technique and of the $\text{Hg}(^3\text{P}_0)$ work have been published. Numerical simulation studies of the quenching and trapping of resonance radiation have reached the point at which there is good agreement with experimental data.

The most interesting new directions are: (i) the use of the phase-shift technique in conjunction with an esr spectrometer; (ii) relaxation studies involving the interconversion of $\text{Hg}(^3\text{P}_0)$ and $\text{Hg}(^3\text{P}_2)$ with the aid of a pulsed tuneable laser.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Properties of Selected Chemical Compounds for Preparation of New Materials
2. PRINCIPAL INVESTIGATOR: Professor Michael T. Pope
Department of Chemistry
Georgetown University
Washington, DC 20007
3. INCLUSIVE DATES: 1 March 1970 to 31 August 1974
4. GRANT NUMBER: AFOSR-70-1833
5. COSTS AND FY SOURCE: \$59,406 FY 70; \$70,619 FY 72
6. SENIOR RESEARCH PERSONNEL: Dr. L. Barcza
Dr. C. M. Flynn, Jr.
Dr. R. A. Prados
7. JUNIOR RESEARCH PERSONNEL: J. J. Altenau S. E. O'Donnell
G. L. Beyer D. P. Smith
P. A. Bushey S. C. Termes
E. L. Bye C. H. Wendel
P. T. Mecklejohn
8. PUBLICATIONS:

"Electron Spin Resonance Spectra of Mixed-Valence Heteropoly Anions," M. T. Pope, D. P. Smith, J. J. Altenau, and J. Bender, Proc. XIII Int. Conf. Coord. Chem., Krakow and Zakopane, 1, 127 (1970)

"Tungstovanadate Heteropoly Complexes. I. Vanadium (V) Complexes with the Constitution $M_6O_{19}^{n-}$ and $V:W = 1:2$," C. M. Flynn, Jr. and M. T. Pope, Inorg. Chem. 10, 2524 (1971).

"Tungstovanadate Heteropoly Complexes. II. Products of Acidification of $V_2W_4O_{19}^{4-}$," C. M. Flynn, Jr. and M. T. Pope, Inorg. Chem. 10, 2745 (1971).

"Heteropoly Complexes: Recent Developments and Prospects," M. T. Pope, Polymer Reprints, 13, 787 (1972).

"Tungstovanadate Heteropoly Complexes. III. The Ion $V_5W_8O_{40}^{7-}$," C. M. Flynn, Jr. and M. T. Pope, Inorg. Chem. 11, 1950 (1972).

"Heteropoly and Isopoly Anions as Oxo Complexes and Their Reducibility to Mixed-Valence 'Blues'," M. T. Pope, Inorg. Chem. 11, 1973 (1972).

"Heteropoly 12-Metallophosphates Containing Tungsten and Vanadium. Preparation, Voltammetry and Properties of Mono-, Di-, Tetra-, and Hexavanado Complexes," D. P. Smith and M. T. Pope, Inorg. Chem. 12, 331 (1973).

- "Optical and ESR Spectra of the 11-Tungstovanado (IV) phosphate Anion. A Heteropoly Blue Analogue," D. P. Smith, H. So, J. Bender, and M. T. Pope, Inorg. Chem. **12**, 685 (1973).
- "Tungstovanadate Heteropoly Complexes. IV. Vanadium(IV) Complexes," C. M. Flynn, Jr. and M. T. Pope, Inorg. Chem. **12**, 1626 (1973).
- "Heteroconjugation of Inorganic Anions in Non-Aqueous Solvents. I. Perchlorate and Halide Complexes of 1,2 Dihydroxybenzene," L. Barcza and M. T. Pope, J. Phys. Chem. **77**, 1795 (1973).
- "Heteroconjugation of Inorganic Anions in Non-Aqueous Solvents. II. Perchlorate Complexes of Some Organic Hydroxy Compounds," L. Barcza and M. T. Pope, J. Phys. Chem. **78**, 168 (1974).
- "ESR Spectrum and Structure of the 5-Tungstovanadate Ion," H. So, C. M. Flynn, Jr. and M. T. Pope, J. Inorg. Nucl. Chem. **36**, 329 (1974).
- "Reduction of 12-Molybdocerate (IV) Anion. The Optical Spectrum of 12-Molybdocerate (III)," L. McKean and M. T. Pope, Inorg. Chem. **13**, 747 (1974).
- "The Nature of Electron Delocalization in a Heteropoly Blue Anion. Evidence for Valence Trapping at Low Temperatures," R. A. Prados, P. T. Meiklejohn, and M. T. Pope, J. Amer. Chem. Soc. **96**, 1261 (1974).
- "Tungstovanadate Heteropoly Complexes. V. The Ion $H_2W_{11}VO_{40}^{7-}$ and the Oxidation and Reduction of Tungstovanadates, C. M. Flynn, Jr., M. T. Pope, and S. O'Donnell, Inorg. Chem. **13**, 831 (1974).
- "13-Vanadomanganate (IV) and Nickelate (IV)," G. B. Kauffman, R. Fuller, J. Felser, C. M. Flynn, Jr. and M. T. Pope, Inorg. Synth. **15**, 103 (1974).
- "Synthesis of Heteropoly Anions in Aprotic Solvents. Tungstoselenates (V), -(VI), and -(VII)," P. T. Meiklejohn, M. T. Pope, and R. A. Prados, J. Amer. Chem. Soc. **96**, 6779 (1974).
- "Heteroconjugation of Inorganic Anions in Non-Aqueous Solvents. III. Complexes of Polymolybdates and -Tungstates with Chloral Hydrate," L. Barcza and M. T. Pope, J. Phys. Chem. **79**, 0000 (1975).
- "Models for Heteropoly Blues. Degrees of Valence Trapping in Vanadium (IV)- and Molybdenum (V)-Substituted Keggin Anions," J. J. Altenau, M. T. Pope, R. A. Prados, and H. So, Inorg. Chem. **14**, 0000 (1975).
- "Stabilization of Uncommon Oxidation States in Heteropoly Complexes, in 'Theory and Structure of Complex Compounds', W. Kakolowicz, ed., Wroclaw, Poland," M. T. Pope, In Press.
- "Studies of the Properties of Selected Chemical Compounds for Preparation of New Materials," Michael T. Pope, Final Technical Report.
- "Oxidation of Catechol by Hexamolybdate," L. Barcza and M. T. Pope, In Press.
- "ESR Studies of Heteropoly Blues," R. A. Prados and M. T. Pope.

"Electron Exchange Rate Between $\text{PMo}^{\text{V}}\text{W}_{11}\text{O}_{40}^{4-}$ and $\text{PMo}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$," S. E. O'Donnell and M. T. Pope.

"Heteropoly Tungstates Containing Re(V), -(VI), and -(VII)," P. T. Meiklejohn, R. A. Prados and M. T. Pope.

"Heteropoly Tungstates Containing OsN^{3+} and RuNO^{3+} ," E. L. Byde, Hoof, M. T. Pope and G. H. Wendel, P. A. Bushey.

"Oxidation and Reduction of Tungsto- and Molybdouranates (IV)," S. C. Termes and M. T. Pope.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Heteropoly oxometallate complexes ("heteropoly anions") of tungsten, molybdenum and vanadium, have been the subject of this research program. The aims have been (a) to synthesize new complexes that might be expected to have unusual properties, and (b) to explore and exploit properties of heteropoly anions in general. The properties of principal interest are those associated with the electronic structures of heteropoly anions: oxidation-reduction (intermolecular electron transfer) properties of new species containing transition metals in uncommon oxidation states; internal electron transfer processes in mixed valence complexes; optical absorption; and magnetic exchange. The structures of heteropoly anions resemble discrete symmetrical fragments of close-packed metal oxide lattices, and the principles underlying the applications of the latter materials (as semiconductors, ferrite magnets, heterogeneous catalysts, lasers, etc.) can be elucidated by study of the former. Not only are heteropoly anions, on account of their solubilities and discrete structures, accessible to study by a broader range of experimental techniques than are the metal oxides, but they may be used in place of the oxides in many applications. Several new heteropoly anions have been prepared, isolated as numerous salts, and characterized by electrochemical and spectroscopic measurements. The heteroatoms in these complexes are: in octahedral coordination by oxygen, Re(V), Re(VI), Re(VII), Os(VI) as OsN^{3+} , Ru(II) and Ru(I) as RuNO^{3+} and RuNO^{2+} ; in icosahedral (12-fold) coordination by oxygen, Ce(III) and U(V), both f¹ species. Rapid, reversible electron transfer reactions involving isostructural pairs of heteropoly complexes have been studied. These reactions involve the following oxidation state changes: $\text{Mo(V)} \longleftrightarrow \text{Mo(VI)}$, $\text{W(V)} \longleftrightarrow \text{W(VI)}$, $\text{V(V)} \longleftrightarrow \text{V(IV)}$, $\text{Re(V)} \longleftrightarrow \text{Re(VI)} \longleftrightarrow \text{Re(VII)}$, $\text{RuNO}^{3+} \longleftrightarrow \text{RuNO}^{2+}$, $\text{Ce(IV)} \longleftrightarrow \text{Ce(III)}$, $\text{U(IV)} \longleftrightarrow \text{U(V)}$. The rate of outer-sphere electron exchange between molybdenum (V, VI) in two heteropoly anions has been measured by esr line-broadening techniques. The electron exchange involves a novel charge transfer complex between the anions which was detected by optical spectroscopy.

The electronic structures of mixed valence heteropoly anions (heteropoly blues) have been probed by esr and optical spectroscopy. Several publications in this area support a model for such complexes in which electrons are weakly trapped on individual metal atoms and are delocalized over the whole structure of the anion by means of a thermally-activated hopping process. The electron delocalization in heteropoly blues is analogous to semiconduction in metal oxides. It has been further proposed by heteropoly blues can be derived (by reduction) only from those heteropoly anions with structures in which the metal atoms are coordinated to a single terminal oxygen atom. All experimental results so far available are consistent with this hypothesis.

Some heteropoly anions have been shown to participate in hydrogen bonding with organic hydroxy compounds to a lesser extent than does the perchlorate anion. However, certain redox reactions involving heteropoly anions in aprotic solvents are found to be kinetically rather than thermodynamically controlled, and in these cases, hydrogen bonding appears to be involved. Thus catechol (1,2 dihydroxybenzene) is oxidized to o-benzo-quinone by $\text{Mo}_6\text{O}_{19}^{2-}$ while p-hydroquinone is unaffected.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Beam Methods of Evaluating High Energy Sources for Advanced Propulsion Systems
2. PRINCIPAL INVESTIGATOR: Dr. E. W. Rothe
Research Institute for
Engineering Sciences
College of Engineering
Wayne State University
Detroit, Michigan 48202
3. INCLUSIVE DATES: 1 September 1969 to 31 July 1974
4. GRANT NUMBER: AFOSR-69-1799
5. COST AND FY SOURCE: \$36,500 FY 69; \$45,797 FY 70; \$45,891 FY 71
\$45,968 FY 72; \$46,439 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. Roger Fenstermaker
Dr. R. K. B. Helbing
Dr. G. P. Reck
7. JUNIOR RESEARCH PERSONNEL: W. M. Jackson
C. B. Leffert
S. Y. Tang
8. PUBLICATIONS:

"Quenching of Glory Undulations: Breathing Sphere Model," R. K. B. Helbing, J. Chem. Phys. 51, 3628 (1969).

"Quenching of Glory Undulations for Scattering from Polyatomic Molecules: Clover-Leaf Model for Spherical Top Molecules," R. K. B. Helbing, J. Chem. Phys. 53, 1547 (1970).

"Glory Scattering of Lithium by a Series of Molecules. III. Spherical Top Molecules," R. K. B. Helbing and E. W. Rothe, J. Chem. Phys. 53, 1555 (1970).

"Glory Scattering of Lithium by a Series of Molecules. IV. Miscellaneous Molecules," E. W. Rothe and R. K. B. Helbing, J. Chem. Phys. 53, 2501 (1970).

"Systematic Error in Beam-Gas Experiments: the Electron Affinity of Br₂," E. W. Rothe and R. W. Fenstermaker, J. Chem. Phys. 54, 4520 (1971).

"Threshold Behavior of Collisional Ionization Processes," R. W. Fenstermaker, W. M. Jackson, C. B. Leffert, E. W. Rothe, Seventh International Conference on the Physics of Atomic and Electronic Collisions (North Holland Publishing Co., Amsterdam, The Netherlands, 1971).

"A Time-of-Flight Chemical-Accelerator for Low Center-of-Mass Energy Spreads," C. B. Leffert, W. M. Jackson, E. W. Rothe and R. W. Fenstermaker, Rev. Sci. Instrum. 43, 917 (1972).

"Measurement of the Electron Affinity of NO_2 ," C. B. Leffert, W. M. Jackson and E. W. Rothe, J. Chem. Phys. **58**, 5801 (1972).

"Cesium Impact Source for Negative-Ion Mass Spectra," S. Y. Tang, E. W. Rothe and G. P. Reck, Int. J. Mass Spectrom, Ion Phys. **14**, 79 (1974).

"Collisional Ionization of Cesium: Relaxation of Product Fragments," S. Y. Tang, E. W. Rothe and G. P. Reck, J. Chem. Phys. **60**, 4096 (1974).

"Anion Production from $\text{Cs} + \text{CF}_3\text{X}$: Evidence for Stripping," E. W. Rothe, S. Y. Tang and G. P. Reck, Chem. Phys. Ltrs. **26**, 434 (1974).

"Negative Ion Formation from Energetic Collisions of Cesium with CO_2 , CS_2 , COS ," S. Y. Tang, E. W. Rothe and G. P. Reck, J. Chem. Phys. **61**, 2592 (1974).

"Collisional Ionization of Cs with SF_6 ," C. B. Leffert, S. Y. Tang, E. W. Rothe and T. C. Cheng, J. Chem. Phys. **61**, 4929 (1974).

"Ionizing Collisions of Cesium with Cl_2 , Br_2 , and I_2 ," S. Y. Tang, C. B. Leffert, E. W. Rothe, J. Chem. Phys. **62**, 132 (1975).

"Ionizing Collisions of Cesium with a Series of Alkyl Iodides," C. B. Leffert, S. Y. Tang, W. M. Jackson and E. W. Rothe, manuscript in preparation.

"Energy Resolution in Heavy Particle Collision Experiments," C. B. Leffert and E. W. Rothe, manuscript in preparation.

"Stripping Reactions with Freons," S. Y. Tang, G. P. Reck and E. W. Rothe, manuscript in preparation.

"Negative Ion Mass Spectra for Several Organic Molecules," S. Y. Tang, G. P. Reck and E. W. Rothe, manuscript in preparation.

"Deconvolution of Heavy Particle Experiment," C. B. Leffert, manuscript in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Colliding particles have been the subject matter of much scientific inquiry. Of interest are the details of naturally occurring particle collisions that are manifest in the bulk properties of matter. Controlled collisions may also probe the structure of the particles themselves. Controlled collision experiments have been a basic tool of science to probe atoms, molecules and nuclei. In this connection projectiles ranging from photons to heavy molecules have been directed toward other bits of matter to explore the basic forces that bind the parts to the whole. In the last century the size of the "fundamental particle" has been repeatedly reduced, by experiments with ever more energetic projectiles, until the particle concept itself is now in doubt. On the other hand, our understanding of the atomic and molecular properties of matter has increased enormously. As an example, molecular collision theory provides a beautiful understanding of such phenomena as mass, momentum, and energy transport. Our understanding of the dynamics of molecular

collisions, however, is incomplete and much useful information is yet to be obtained. The research described here presents the results of collision experiments. These were designed so that molecular properties could be extracted from analysis of the products from two colliding molecular beams.

The research falls into three separate categories:

Theoretical analysis of glory scattering experiments.

Experimental collision studies at kinetic energies between 1-10eV (development of a chemical accelerator for measurements of ionization phenomena) with very high energy resolution.

Experiments with higher energies (20-400eV) in order to study negative ion properties.

In the experiments at higher energy negative ions were produced in a single-collision charge-transfer source. A beam of cesium atoms with kinetic energies which were variable between 10 and 350 eV intersected a beam of target molecules. Negative ions and Cs^+ were formed. The energy dependence of these anion spectra were measured for SO_2 , CH_3NO_2 , SF_6 , and CF_2Cl_2 . The observed cesium impact spectra were qualitatively different from those produced by electrons. At the higher cesium-atom energies, they were relatively insensitive to energy. Large parent ion intensities were seen for SO_2 and CH_3NO_2 . For $\text{Cs}+\text{SF}_6$, ratios ($\text{SF}_6^-/\text{SF}_5^-$) and F^-/SF_5^-) were in agreement with those of Compton and Cooper for the limited range of Cs energy employed in both experiments.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Energy Transfer Processes in Gas Laser Materials
2. PRINCIPAL INVESTIGATOR: Dr. D. J. Seery
United Technologies Research Center
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 16 March 1969 to 14 May 1975
4. CONTRACT NUMBER: F44620-69-C-0100
5. COSTS AND FY SOURCE: \$37,014 FY 69; \$36,990 FY 70; \$36,988 FY 71
\$36,991 FY 72; \$18,500 FY 73; \$31,285 FY 74;
\$23,996 FY 75

6. RESEARCH PERSONNEL: D. J. Seery

7. PUBLICATIONS:

"On a Shock-Tube Study of Carbon Dioxide-Carbon Monoxide Vibrational Energy Transfer," D. J. Seery, J. Chem. Phys. v56, 631-637 (1972).

"Chemistry of Pollutant Formation in Flames," H. B. Palmer and D. J. Seery, J. Ann. Rev. of Phys. Chem. v24, 235-262 (1973).

"Vibrational Relaxation of Hydrogen Chloride with Inert Gas Collision Partner," D. J. Seery, J. Chem. Phys. v58, 796-1799 (1973).

"Intramolecular Energy Transfer in Carbon Dioxide," D. J. Seery, J. Chem. Phys. v56, 4714-4715 (1972).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major efforts in this program were directed toward an understanding of vibration-vibration and vibration-translation energy transfer for collision partners of interest to high-powered infrared lasers. These studies have all been carried out using the shock tube - infrared emission technique.

The experimental program can be subdivided according to the following subjects:

1. A study of the V-V transfer between CO₂(001) and CO. This work has been published under the title "On a Shock Tube Study of CO₂-CO Vibrational Energy Transfer," J. Chem. Phys. 56, 531 (1972).
2. An experimental measurement of the intramolecular energy transfer in CO₂ which demonstrated the compatibility of the shock tube - infrared emission and the laser fluorescence techniques. This work has been published under the title "Intramolecular Energy Transfer in CO₂," J. Chem. Phys. 56, 4714 (1972) and was presented at the 161st National Meeting of the ACS, Los Angeles, March 1971.
3. Measurements of the V-T relaxation rate of HCl in the presence of inert gases. This work has been published as "Vibrational Relaxation of HCl with Inert Gas Collision Partners," J. Chem. Phys.

58, 1796 (1973).

4. Measurements of the V-V and V-T energy transfer in HCl-CO collisions. This work involved extensive analytical modelling as well as the experimental shock tube study. A paper based on this work has been presented at the 164th National Meeting of the ACS, New York, 1972 and a more complete version of the work is to be published in the Journal of Chemical Physics.

5. Minor studies have been carried out on the V-V transfer in N_2O -CO mixtures and V-T transfer in pure NO and a literature search on combustion chemistry and air pollution. This work has been published under the title "Chemistry of Pollutant Formation in Flames" in Ann. Rev. Phys. Chem. 24, 235 (1973).

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Properties and Reactions of Atomic Species Generated at High Temperatures.

2. PRINCIPAL INVESTIGATOR: Dr. Philip S. Skell
Department of Chemistry
Penn State University
University Park, Pennsylvania

3. INCLUSIVE DATES: 1 November 1970 - 30 September 1974

4. GRANT NUMBER: AFOSR-71-1983

5. COSTS AND FY SOURCE: \$98,342 FY71; \$99,014 FY72; \$99,386 FY73; \$94,227 FY74

6. SENIOR RESEARCH PERSONNEL:	Dr. R. Davidson	Dr. M. McGlinchey
	Dr. J. C. Day	Dr. M. Silvon
	Dr. J. E. Dobson	Dr. H. Takeucki
	Dr. J. Girard	Dr. T. Terasowa
		Dr. M. Yevitz

7. JUNIOR RESEARCH PERSONNEL:

D. Adams	W. McHale
W. Brent	P. Owen
F. Fagone	D. Pohl
J. Hovel	J. Seehafer
K. Hess	K. Shea
D. Howe	S. Stodola
D. Hwang	S. Valenty
S. Lander	J. Villaume
S. Love	L. Wood

8. PUBLICATIONS - (All with P. S. Skell as co-author):

"Reactions of Atomic Silicon II: Observations on the Reactivity of Silene Intermediates", P. W. Owen, Tet. Lett., 18, 1807 (1972).

"Reaction of Nickel Atoms with Unsaturated Hydrocarbons", J. J. Havel, M. J. McGlinchey, D. W. Smith, Chem. Comm., 1972, 1098.

"Fragmentation Reactions of Three-Membered Rings Induced by Carbon Atoms", J. E. Villaume, J. Amer. Chem. Soc., 94, 3455 (1972).

"Reactions of Iron Atoms with Unsaturated Hydrocarbons", D. L. W-Smith, L. R. Wolf, J. Amer. Chem. Soc., 94, 3455 (1972).

"Some Reactions of Ground State Magnesium Atoms", J. E. Girard, J. Amer. Chem. Soc., 94, 5518 (1972).

"Anchimeric Assistance in Radical Bromination of Bromoalkanes. Contradiction of Claims by Tanner, et al.", K. J. Shea, J. Amer. Chem. Soc., 94, 6550 (1972).

"The Chemistry of Atomic Silicon III: Reactions of Electron Bombardment Produced Silicon Vapor with Silanes", P. W. Owen, J. Amer. Chem. Soc., 94, 5434 (1972).

"Bridging in β -Haloalkyl Radicals. A critique of Published Criticisms", K. J. Shea, Israel Journal of Chemistry, 10, 493 (1972).

"Reactions of Free Aluminum Atoms, Direct Synthesis of Organoaluminum Compounds", L. R. Wolf, J. Amer. Chem. Soc., **94**, 7919 (1972).

"Deoxygenation of Cyclopropanecarboxaldehyde and Cyclopropylmethylketone", J. H. Plonka, Tetrahedron, **28**, 3571 (1972).

"The Reaction of Atomic Nitrogen with Propane", J. J. Havel, J. Org. Chem., **37**, 3744 (1972).

"Free Carbonium Ions" in Vol. 2 of "Carbonium Ions", J.T. Keating, John Wiley and Sons, G. A. Olah and P. Von R. Schleyer, eds. N.Y. 1970, pp. 573-653.

"Potential Surfaces for the Addition of CH_2 and CF_2 to Ethylene and Isobutene", R. Hoffmann and D. M. Hayes, J. Phys. Chem., **76**, 664 (1972).

"Chromium Atoms in Organometallic Synthesis", D. L. Williams-Smith and M. J. McGlinchey, J. Amer. Chem. Soc., **95**, 3337 (1973).

"Chemistry and the Carbon Arc", J. J. Havel and M. J. McGlinchey, Acc. Chem. Res., **6**, 97 (1973).

"Deoxygenation and Desulfurization of Cyclic Ethers and Thioethers by Carbon Atoms. Intermediates with Excess Energy in a Low-Temperature Matrix, K. J. Klabunde, J. H. Plonka, J. S. Roberts and D. L. Williams-Smith, J. Amer. Chem. Soc., **95**, 1547 (1973).

"Stereospecific Radical-Chain Exchange of Hydrogens", K. J. Shea, J. Amer. Chem. Soc., **95**, 283 (1973).

" α -Mercuricarbenes. Synthesis of α -Mercuricyclopropanes. Elimination of Wolff Rearrangement in Acylcarbenes", S. J. Valenty, J. Amer. Chem. Soc., **95**, 5042 (1973).

"Relaxation of Excited State Carbene to Ground State. An Internal Heavy Atom Effect", S. J. Valenty, J. Amer. Chem. Soc., **95**, 5041 (1973).

"Chemical Synthesis" R. A. Davidson, Encyclopaedia Britannica, 208 (1972).

"1,4-, 1,5-, and 1,6-Dibromoalkanes from Ionic Reaction of Bromine with n-Butylcyclopropane", J. C. Day and K. J. Shea, J. Amer. Chem. Soc., **95**, 5089 (1973).

"Photobromination of Alkylcyclopropanes. Stereochemistry of Homolytic Substitution at a Saturated Carbon Atom", K. J. Shea, J. Amer. Chem. Soc., **95**, 6728 (1973).

"Bridged Bromine and Chlorine Free-Radical Intermediates. Free-Radical Halogenations of 2-Halobutanes", R. R. Pavlis, D. C. Lewis, K. J. Shea, J. Amer. Chem. Soc., **95**, 6735 (1973).

"Carbon Scrambling in C_5H_5^+ , C_5H_6^+ , and C_7H_7^+ Produced by Electron Bombardment", R. A. Davidson, J. Amer. Chem. Soc., **95**, 6843 (1973).

"Anchimeric Assistance in Photobromination of Alkyl Halides", K. J. Shea and D. C. Lewis, J. Amer. Chem. Soc., **95**, 7768 (1973).

"Bridged Free Radicals", K. J. Shea in "Free Radicals", Vol 2, J. K. Kochi, Ed., New York, N. Y., 1973, Chap 26, p. 809.

" α -Diazomercurials, Synthesis and Photochemistry", S. J. Valenty, J. Org. Chem. **38**, 3937 (1973).

"Reactions of Tungsten and Molybdenum Atoms with 1,3-Butadiene. Tris(butadiene) tungsten and -molybdenum", E. M. VanDam and M. P. Silvon, J. Amer. Chem. Soc., **96**, 626 (1974).

"Reactions of Molybdenum and Tungsten Atoms. Synthesis of Bisarene Sandwich Compounds", M. P. Silvon, E. M. VanDam, J. Amer. Chem. Soc., **96**, 1945 (1974).

"The Formation and Reactions of Monovalent Carbon Intermediate. III. The Reaction of Carbethoxymethyne with Olefins", O. P. Strausz, G. J. A. Kennepohi, F. X. Garneau, Thap DoMinh, B. Kim, S. Valenty and P. S. Skell, J. Amer. Chem. Soc., **96**, 5723 (1974).

"Properties of Reaction Atomic Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances", P. S. Skell, Fin. Tech.Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research is to devise methods of carrying out free atom reactions under terrestrial conditions and thereby to describe the reaction chemistry of all the atoms. In doing so, in some instances new substances are synthesized and better synthesis of known substances become available. With few exception vacuum vaporizations of the high boiling elements leads to the free atom (in all cases for the transition metals). Useful rates of vaporization are generally attained at temperatures where the equilibrium vapor pressure is 10^{-3} torr. For the transition metals this requires temperatures between 1200-3500°. Each element presents a new problem in the details of effective procedure. Up to 1800° in many instances ceramic crucibles can be used as containers. For tungsten and molybdenum, resistive heating of suitably doped wires has been effective. For platinum, coated tungsten wires are serviceable. For boron, silicon and rhenium, electron bombardment of the element on a water-cooled copper hearth was necessary.

Most substrates and products decompose at temperatures far below the vaporization temperatures. Since in addition, fast deactivation of hot products was deemed necessary, the effort has been focused on ensuring low temperature, condensed phase contact between atoms and substrate. High dilution is also a requirement, since recombination of metal atoms is an exothermic reaction to be avoided. These were the considerations in the carbon atom research and the methods learned there have served in the examination of other high boiling elements.

The distance between hot and cold regions is 2-4 inches, the pressure is maintained below 10^{-4} torr to preclude gas phase collisions, and metal atoms and substrate molecules are deposited simultaneously on a surface cooled with liquid nitrogen; reactions take place in this cold solid. After, the co-deposition products are worked up by sublimation, extraction, etc., as dictated by the properties of the products.

Recently it was found to be advantageous to co-deposit the atoms with substances which are mildly complexing, and then adding a more reactive substrate to this matrix.

Phase 1 for the metal atoms consisted of a survey in which each metal was examined in a small number of experiments, often only one, the reaction of the metal atom with propene at liquid nitrogen temperatures. After removing the excess substrate at -78° the residue was treated with D₂O which dis-

placed or hydrolyzed the organic portions of the organometallic products which had been made. The hydrocarbons released were analyzed to determine their identities, amounts, and extents of deuteration. The elements examined were B, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Pd, Ag, Sn, Tb, Dy, Er, W, Re, Pt, Au, Pb, and U.

With the exception of those elements underlined, organometals which are stable at -78° are formed. After hydrolysis, with elements such as aluminum the products are alkanes; with nickel and palladium, alkenes. The alkanes are dideuterio compounds, the alkenes were usually deuterated to small extents. With higher olefins isomerization of the double bond position occurred rapidly with the first row transition metals. As could be anticipated, the pattern of products and extents of deuteration were different for each of the elements, and it is now abundantly clear that a separate study of each element will be required if the goal goes beyond the broadest of generalizations.

Much of the current work can be described as phase 2, completed or being actively attacked for 13 elements listed for the phase 1 studies. In this phase each element is studied in some ten to fifteen reactions, using a variety of substrates: water, ammonia, phosphorous trifluoride, alkyl halides, olefins, diolefins, acetylenes, and aromatic compounds; occasionally substrates such as NO, CO and CO₂ have been employed. As experience was gained, the sophistication of the experiments has improved, and consequently the quality of the discoveries have been more gratifying. The elements studied in phase 2 are (underlined if published): B, Mg, Al, So, Cr, Fe, Co, Ni, Mo, Pd, W, Re and Pt.

The nature of this work is best illustrated by the most recent set of experiments with tungsten and molybdenum atoms. Tungsten and molybdenum are remarkably similar in that they show the same types of reactions. With 1,3-butadiene they form remarkably stable tris-butadiene tungsten and molybdenum. These compounds appear to be unique in organometal chemistry since no other tris-butadiene metal compounds are known. X-ray examination of the tungsten compound indicates a structure in which cisoid butadienes are positioned as a girdle around the metal atom, probably π -bonded. With arenes these metal atoms form bis-arene sandwich compounds, the arenes being substituted with groups such as $-\text{OCH}_3$, $-\text{COOCH}_3$, $-\text{N}(\text{CH}_3)_2$, F, Cl, etc. Thus a range of bis-arenes are available which heretofore were neither known nor accessible by the other methods. With cyclopentadiene, the bis-cyclopentadienyl metal dihydrides are readily prepared. Bis-arene types have been prepared in which one side of the sandwich is a seven ring, the other a five ring.

Phase 3 experiments have been done mainly with C₁, C₂, and C₃, where concern was focused on the mechanisms of reactions; most of that work is published. The work along these lines with silicon atoms has also been published.

With nickel atoms and deuterated propenes it was established that rearrangements occur by conversion of the π -complex to the π -allyl nickel hydride, rather than the elimination-readdition mechanism.

For a number of atoms, boron and more reactive metals, attempts are being made to understand the mechanism of hydrogen release on reaction with water. There are some remarkable isotope effects, some being very large, similar to what has been reported for reactions of electrons with water.

With aluminum atoms and non-terminal olefins it is believed that the first examples of compounds with Al-Al bonds have been made.

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Processes Controlling Energy Transfer
2. PRINCIPAL INVESTIGATOR: Professor E. W. Schlag
Institute for Physical Chemistry
Technical University, Munich
Munich, Germany
3. INCLUSIVE DATES: 1 November 1971 - 31 July 1974
4. GRANT NUMBER: AFOSR-72-2181
5. COSTS AND FY SOURCE: \$50,379 FY72
6. SENIOR RESEARCH PERSONNEL: Dr. J. G. Larson
7. JUNIOR RESEARCH PERSONNEL: Willis Howard
H. L. Seirgle
S. Schneider

8. PUBLICATIONS:

"Single Photo Phase Fluorimetry with Nanosecond Time Resolutions", E. W. Schlag, H. L. Seirgle, S. Schneider, J. G. Larson, Review of Scientific Instruments, **45** 364 (1974).

"Direct Timing of Lifetimes of Vibrationally Excited Molecules Before Decay by Radiation, Intersystems Crossing, or Collisions. High Resolution Lifetime Measurement". E. W. Schlag, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The emission of coherent electromagnetic radiation from laser systems is preceded by complex, rapid processes of energy transfer, redistribution, storage, and release at the molecular level. This research sought to identify and measure the time duration of processes whose understanding and control is the key to advances in laser technology. To get a fundamental understanding of primary photophysical processes which occur after the absorption of light, one has to have reliable rate data for well defined microscopic processes as a function of the quantum states of the molecular system of interest. This implies, that one must prepare the quantum states with good energy resolution and second, that one must employ a timing apparatus, which can operate on a time scale of 10^{-6} to 10^{-8} seconds in order to get kinetic data by direct timing of the fluorescence.

A method was developed for correlating phase excitation with a response of single photons. The correlation spectrometer was constructed in conjunction with a xenon light source and a monochromator. The limiting resolution commensurate with adequate signal strength was 10 reciprocal centimeters. A new method was initiated to enable one to make high resolution measurements of dynamic processes. High resolution was here defined as being in the picometer range, i.e., limited only by the Doppler profile of the line, analogous to the high resolution spectral information now available. Laser was constructed which could be narrowed and doubled to meet the needed requirements. The tunable dye laser was of the flash pumped design, and it was further decided to measure all absorption and emission parameters for each individual flash, employing a variable length folded path cell. In this way, all kinetic parameters were determined. The output of the laser system was so high that a single flash was satisfactory for a complete determination of all kinetic parameters.

COMPLETED PROJECT SUMMARY

1. TITLE: Absorption and Collisional Redistribution of Molecular Energy Revealed by Double Resonance Spectroscopy/
Molecular Deactivation Processes in Visible Chemical Laser Systems
2. PRINCIPAL INVESTIGATOR: Dr. J. I. Steinfeld
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 February 1971 to 31 August 1974
4. GRANT NUMBER: AFOSR-71-2032
5. COSTS AND FY SOURCE: \$42,000 FY 71; \$47,619 FY 72
\$27,000 FY 73; \$46,379 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. S. G. Kukolich
Dr. L. Marabella
Dr. A. C. Nelson
Dr. J. H. S. Wang
7. JUNIOR RESEARCH PERSONNEL: D. S. Frankel R. Micheels
B. Garetz A. V. Nowak
P. L. Houston D. J. Ruben
A. Kotlar M. Robinson
J. M. Levy R. W. Stearns
8. PUBLICATIONS:

"Behavior of a Pulsed-Discharge Laser with an Intracavity Absorber,"
P. L. Houston, D. G. Sutton and J. I. Steinfeld, J. Appl. Phys. 43,
2014 (1972).

"Energy Transfer Processes," J. I. Steinfeld, MTP Biennial Reviews
of Science, Technology and Medicine, Reaction Kinetics Vol. 9,
p. 247-269 (J. C. Polanyi, Ed.), MTP-Butterworths, Aylesbury, 1972.

"Infrared Double Resonance in BCl_3 ," P. L. Houston, A. V. Nowak and
J. I. Steinfeld, Proc. VIIth Internatl. Quantum Electronics Conf.,
p. 89, (Montreal, Quebec, May 1972).

"Microwave Transient Nutation Measurements of Relaxation on OCS and
 NH_3 ," J. H. S. Wang, J. M. Levy, S. G. Kukolich and J. I. Steinfeld,
Chem. Phys. 1, 141 (1973).

"Transient Nutation Effects in Time-Resolved Infrared-Microwave
Double Resonance in Ammonia," J. M. Levy, J. H. S. Wang, S. G.
Kukolich and J. I. Steinfeld, Phys. Rev. Ltrs. 29, 395 (1972).

"Infrared Double Resonance in Boron Trichloride," P. L. Houston,
A. V. Nowak and J. I. Steinfeld, J. Chem. Phys. 58, 3373 (1973).

"Near-Resonant Vibration-Rotation Energy Transfer," Lise-Lotte Poulsen, P. L. Houston and J. I. Steinfeld, J. Chem. Phys. 58, 3381 (1973).

"Self-Broadening of Infrared Absorption Lines in Propynal," A. V. Nowak and J. I. Steinfeld, J. Chem. Phys. 57, 5595 (1972).

"Time-Resolved Infrared-Microwave Double Resonance in Ammonia," J. M. Levy, J. H. S. Wang, S. G. Kukolich and J. I. Steinfeld, Bull. Amer. Phys. Soc. (Ser. II) 18, 62 (1973).

"Direct Observation of Rotational Energy Transfer in Ammonia by Time-Resolved Infrared-Microwave Double Resonance," J. M. Levy, J. H. S. Wang, S. G. Kukolich and J. I. Steinfeld, Chem. Phys. Ltrs. 21, 598 (1973).

"Molecular Beam Laser Measurements of Relaxation Cross Sections in NH_3 ," S. G. Kukolich, J. H. S. Wang and D. E. Oates, Chem. Phys. Ltrs. 20, 519 (1973).

"Microwave Transient Nutation and Infrared-Microwave Double Resonance Spectroscopy," J. I. Steinfeld, Proc. Colloque International No. 217 du C.N.R.S., "Methods de Spectroscopie sans Largeur Doppler de Niveaux Excites de Systemes Moleculaires Simples," p. 147 (Aussoix, France, May 1973).

"Infrared-Microwave Double Resonance and Transient Nutation Spectroscopy," J. I. Steinfeld and J. H. S. Wang, Proc. 3rd Vavilov Conference on Nonlinear Optics, Novosibirsk, USSR, June 1973 (in press).

"Near-Resonant Vibration-Rotation Energy Transfer," L. L. Poulsen, P. L. Houston and J. I. Steinfeld, Proc. VIIIth Internatl. Conf. on Physics of Electronic and Atomic Collisions, Vol. I, p. 61 (Institute of Physics, Beograd, Yugoslavia, July 1973).

"Optical Analogues of Magnetic Resonance Spectroscopy," J. I. Steinfeld, "Chemical Applications of Lasers," C. B. Moore, Ed., (Academic Press, New York), 1974.

"Energy Transfer Processes in Monochromatically Excited Iodine. IX. Classical Trajectory and Semiclassical Calculation of Vibrationally and Rotationally Inelastic Cross Sections," M. Robinson, B. Garetz and J. I. Steinfeld, J. Chem. Phys. 60, 3082 (1974).

"Entropy Analysis of Product Energy Distributions in Nonreactive Inelastic Collisions," M. Robinson and J. I. Steinfeld, Chem. Phys. 4, 467 (1974).

"Classical Trajectory and Semiclassical Calculations of Energy Transfer Involving an Electronically Excited Molecule," M. Robinson, Technical Report (July, 1974).

"Potential Surface Crossing in Classical Trajectory Calculations: Application to Collision-Induced Predissociation in Electronically Excited I_2 ," B. Garetz, M. Robinson and J. I. Steinfeld, Chem. Phys. Ltrs. (in press).

"Temperature Dependence of Near-Resonant Vibration-Rotation Energy Transfer," D. Frankel, J. I. Steinfeld, R. D. Sharma and L. L. Poulsen, Chem. Phys. Ltrs. (in press).

"Spectroscopic Measurements of Energy Transfer by Fluorescence and Double Resonance," R. G. Gordon and J. I. Steinfeld, Proc. Israel Scientific Research Conference on Molecular Energy Transfer, Ein-Bogeq, December, 1973 (in press).

"Low-Temperature Absorption Contour of the ν_3 Band of SF_6 ," P. L. Houston and J. I. Steinfeld, J. Mol. Spectroscopy (in press).

"Absorption and Collisional Redistribution of Molecular Energy Revealed by Double Resonance Spectroscopy/Molecular Deactivation Processes in Visible Chemical Laser Systems," J. I. Steinfeld, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Two major areas of investigation were comprehended by this research program. The first was an investigation of vibrational relaxation properties of small polyatomic molecules, primarily by the techniques of infrared-infrared and infrared-microwave double resonance spectroscopy. At a later stage, the emphasis was shifted to deactivation processes involving electronically excited states of small molecules having potential applications to visible chemical laser systems. A number of results were obtained in both areas.

1. Infrared Double Resonance in BCl_3 . Vibrational relaxation of BCl_3 by He, Ne, Ar, Kr, Xe, HCl, DCl, H_2 , HD, D_2 , CH_3F , CHCl_3 and BCl_3 itself was measured by the infrared double resonance technique. The rare-gas transition probabilities are well predicted by the same Tanczos-Stretton breathing-sphere model that was successful for interpreting the analogous results in SF_6 ; a value of $200\text{--}240\text{ cm}^{-1}$ for the average amount of energy removed per collision corresponds to the lowest (e') fundamental vibration of the molecule. The high efficiencies observed for H_2 , HD, HCl and DCl are due to vibration \leftrightarrow rotation energy transfer. These transition probabilities are not well predicted by the existing theory of V-R transfer, but can be calculated from a new near-resonant V-R theory described below. The transfer of vibrational energy from $^{11}\text{BCl}_3$ to $^{10}\text{BCl}_3$ proceeds by a complicated combination of direct (resonant vibration \leftrightarrow vibration) and indirect (vibration \leftrightarrow translation \leftrightarrow vibration) processes. The intermolecular redistribution of vibrational energy by these processes appears to proceed very nearly as fast as intramolecular energy redistribution.

2. Near-Resonant Rotation \leftrightarrow Vibration Energy Transfer. Previous treatments of rotation-vibration energy transfer have used a simple classical rotor model. We have used the method of Rapp and Golden (originally developed for near-resonant vibration-vibration energy exchange) to describe the near-resonant transfer of energy between a quantum rotor. The resulting expression is

$$P(v, v') = \sum_J \sum_{J'} \int du f(u) (2J+1)^{-1} \sum_{M=-J}^{+J} \sin^2 \left[\frac{\pi u V(v', J', M; v, J, M)}{4h (\pi \alpha/8)} \right] \\ \times \text{sech}^2 \left[\frac{\pi \gamma (v', J'; vJ)}{4u (\pi \alpha/8)} \right]$$

where $f(J)$ and $f(u)$ are Boltzman distributions in rotational state J and relative velocity u ; $V(v', J', M' vJM)$ is the matrix element of the intermolecular potential; γ the resonance energy defect between rotation compound state (v, J) and final state (v', J') ; m the collision reduced mass and α the exponential range parameter of the potential. While this model correctly predicts the magnitudes and relative efficiencies of the deactivation rates for BCl_3 by HCl and DCl , it does not reproduce the observed temperature dependence. The latter results can be explained by a long-range-force model, as in the theory of Sharma and Brau.

3. Infrared Saturation and Line Broadening. From the pressure dependence of the absorption of the $\text{P}(12)$ CO_2 laser line by propynal ($\text{HC} \equiv \text{C-CHO}$), we have determined a self-broadening cross section for the absorption line of $(400 + 150) \text{ Å}^2$. The large magnitude of this cross section reflects the long-range dipole forces responsible for the broadening. We have also determined the response of propynal, PF_5 , and BCl_3 to high-intensity laser pulses. With the exception of BCl_3 at high pressures, the absorption data fit the linear saturation model previously applied to SF_6 .

4. Infrared-Microwave Double Resonance in NH_3 , and Transient Microwave Nutation. When the $(J = 8, K = 7)$ rotational level of NH_3 is pumped away from equilibrium by a pulse from a tuned N_2O laser, the microwave absorption intensity in the inversion doublet of that level relaxes as an exponentially-damped sinusoidal oscillation. These oscillations can be understood as a transient nutation of coherently excited molecules. By the use of the Feynman-Vernon-Hellwarth representation, the ammonia inversion levels can be described as an equivalent spin - $1/2$ system. Use of the Bloch phenomenological equations then leads to an explicit form for the relaxation of the microwave signal. Measurements of the pressure dependence of this signal gives a value for the transverse relaxation time T_2 , which can then be compared with the conventional microwave line broadening cross section. Equivalent phenomena can be attained by nonadiabatically switching the molecules in and out of the resonance by means of an applied Stark voltage. Microwave transient nutation experiments of this type have been carried out on the $J = 1 \rightarrow 2$ transition in OCS . The measured T_2 in this case appears to be longer than the corresponding relaxation time as determined in conventional line-broadening experiments.

When inversion levels in NH_3 other than that directly pumped by the N_2O laser are observed in microwave absorption, transient signals having a simple exponential shape are seen. From analysis of these signals we obtained a rotational relaxation rate about one-fifth as large as the coherence decay rate obtained from the T_2 measurements. In a molecular beam maser experiment, it was found that the scattering cross section is greater for a pure inversion state in ammonia than for a coherent superposition state. While this result does not directly imply that T_1 is faster than T_2 under these conditions, it does mean that one must be extremely careful in interpreting relaxation times for different types of experiments.

5. Classical Trajectory Calculations of Energy Transfer in Electronically Excited Molecules. An extensive series of classical trajectory calculations has been completed for I_2 colliding with monatomic gases. Vibrationally and rotationally inelastic cross sections were calculated for I_2 in $v' = 15, 25, 43$, and 50 , with

He, Ne, Ar, Kr, and Xe, and agree in essentially every detail with the experimental results derived from monochromatically excited fluorescence studies. We also investigated a semiclassical approximation ("MITFITS") which yields simple closed-form expressions for these cross sections, but at some sacrifice in accuracy. These calculations have been extended to incorporate the effects of crossing from one potential surface to another as a result of quenching interactions. Several different approximations for doing this are being evaluated. Initial results were once again in quite good agreement with experiment; this work is being continued and extended under renewed AFOSR sponsorship.

6. Linear Entropy Analysis of Inelastic Processes. The "surprisal analysis", recently introduced by Professor R. Levine of the Hebrew University, has proven very useful in interpreting product state distributions in exothermic reactions. The surprisal, $I(f_E)$ is given by

$$I(f_E) = -\ln[P(f_E)/P^O(f_E)]$$

where f_E is the fraction of the available energy in a given final state, and $P^O(f_E)$ is an a priori product distribution, usually taken to be a statistical one. It is often found that linear surprisal plots are obtained, that is

$$I(f_E) = \lambda f_E + (\text{const.})$$

where λ is a "temperature-like" parameter, with $T_{\text{eff}} = E_{\text{available}}/k_B\lambda$. We have applied the surprisal analysis to the vibrational and rotational deactivation data we have for I_2^* , and have found that a small number of λ parameters suffices to characterize all the inelastic collision probabilities.

AFOSR Program Manager: J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Solute-Solvent Interactions and Preferential Solvation:
An NMR Study

2. PRINCIPAL INVESTIGATOR: Dr. Thomas R. Stengle
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

3. INCLUSIVE DATES: 1 October 1971 to 31 October 1974

4. GRANT NUMBER: AFOSR-72-2202

5. COSTS AND FY SOURCE: \$20,000 FY 72; \$10,000 FY 74

6. SENIOR RESEARCH PERSONNEL: Dr. Thomas R. Stengle

7. JUNIOR RESEARCH PERSONNEL: Harvey A. Berman

8. PUBLICATIONS:

"Nuclear Magnetic Resonance Studies of Solvation of Halides: ¹⁹F
Studies of Solvent and Counterion Effects on Chemical Shift,"
James P. K. Tong, Cooper H. Langford, and Thomas R. Stengle,
Can. J. Chem. 52, 1721 (1974).

"Contact Ion Pairing of Perchlorate Ion: A ³⁵Cl NMR Study. I.
Solutions in Pure Solvents," Harvey A. Berman and Thomas R. Stengle,
J. Phys. Chem. May, 1975 (in press).

"Contact Ion Pairing of Perchlorate Ion: A ³⁵Cl NMR Study. II.
Solutions in Mixed Solvents," Harvey A. Berman and Herman Y. C. Yeh
and Thomas R. Stengle, J. Phys. Chem., in press.

"Solute-Solvent Interactions and Preferential Solvation: An NMR
Study, Final Scientific Report, Thomas R. Stengle.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The object of this research was to study the interactions between ion and solvent and between ion and ion in electrolyte solutions in pure and mixed solvents. The primary concern was the development of new methods to determine the composition of the primary solvation shell of ions in solution. The solvation shell may contain solvent molecules and other ions. The former comes under the category of preferential solvation, while the latter is under ion pairing.

The study of preferential solvation was extended to include fluoride ions in mixed solvents. Here the NMR chemical shift of the fluorine nucleus was used as the experimental probe. In mixtures of water with dipolar aprotic solvents, the water is always the preferred component of the solvation shell. When the water is mixed with protic solvents such as alcohols, the solvation shell composition is more random, containing both components. This is probably the effect of the role of hydrogen bonding in fluoride ion solvation; the exact role of hydrogen bonding has not yet been determined.

A new method was developed for the detection of contact ion association in solutions of perchlorates. This method is based on the NMR relaxation time of the chlorine nucleus in the perchlorate ion. This technique enables one to answer some long standing questions concerning the existence of contact ion pairs in certain systems. Those properties of the solvent which are most important in promoting contact ion association have been discovered and the effect of solvent composition in systems of mixed solvents have been elucidated.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: New Perfluoropolymer-Forming Reactions.
2. PRINCIPAL INVESTIGATOR: Dr. Madeline S. Toy
Stanford Research Institute
Menlo Park, California 94025
3. INCLUSIVE DATES: 1 March 1974 - 30 June 1975
4. CONTRACT NUMBER: F44620-74-C-0064
5. COSTS AND FY SOURCE: \$16,999 FY74; \$50,029 FY75
6. SENIOR RESEARCH PERSONNEL: Roger S. Stringham
7. JUNIOR RESEARCH PERSONNEL: None.
8. PUBLICATIONS:

"Photochemical Reactions of Fluoroxyperfluoroalkanes with Perfluorocycloolefins", M. S. Toy and R. S. Stringham, J. Fluorine Chem., 5, 481 (1975).

"A New Synthetic Route for Bis(perfluoro-t-butyl)peroxide and Photolysis with Perfluorocycloolefins", M. S. Toy and R. S. Stringham, submitted to J. Fluorine Chem.

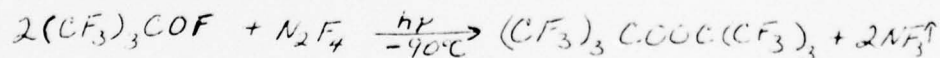
"2,2'-Perfluorodimethoxydicycloalkyls", M. S. Toy and R. S. Stringham, submitted to J. Fluorine Chem.

"New Perfluoropolymer-Forming Reactions", M. S. Toy, Fin. Tech Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to establish polymer forming reactions that could be utilized to synthesize perfluoropolymers with elastomeric properties over a broad temperature range. The principal lines of research activity pursued included studies of (1) the nature of OF bond dissociations and additions, (2) new perfluoropolymer-forming reactions and (3) synthesis of certain monomers and monomer precursors.

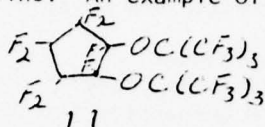
Under photolysis, the homolysis of the OF bond $(CF_3)_3COF \rightarrow (CF_3)_3CO^\bullet + F^\bullet$ was demonstrated in the presence of N_2F_4 which dissociates into NF_2^\bullet radical to function as the fluorine atom acceptor.



In the absence of photolysis, $(CF_3)_3COF$ does react with N_2F_4 at $-60^\circ C$ to form a white solid (I), with a m.p. of about $150^\circ C$.



A new method was discovered for synthesizing vicinal perfluorodi-*t*-butoxycycloalkanes (II) by low temperature photolysis of $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$ and perfluorocycloolefins. An example of II is shown below:



Attempts at the synthesis of the diol $\text{HO}(\text{CF}_3)_2\text{C}(\text{CF}_2)_6\text{C}(\text{CF}_3)_3\text{OH}$ from $\text{Br}(\text{CF}_2)_6\text{Br}$ gave low yields of the product.

AFOSR Program Manager: A. J. Matuszko

COMPLETE PROJECT SUMMARY

1. TITLE: Organolanthanides and Organoactinides Related to Catalysis
2. PRINCIPAL INVESTIGATOR: Dr. Minoru Tsutsui
Department of Chemistry
Texas A & M University
College Station, Texas 77843
3. INCLUSIVE DATES: 1 January 1971 - 31 December 1974
4. GRANT NUMBER: AFOSR-71-2017
5. COSTS AND FY SOURCES: \$25,000 FY 71; \$23,786 FY 72; \$25,000 FY73; \$20,000 FY74
6. SENIOR RESEARCH PERSONNEL: Dr. A. Gebala
Dr. C. Hyde
Dr. G. Voecks
7. JUNIOR RESEARCH PERSONNEL: D. Birkelbach J. John
N. Ely M. Makita
C. Hudman
8. PUBLICATIONS:

"Organolanthanides and Organoactinides. IV. Tricyclopenta-dienylphenyluranium (IV)", A. E. Gebala and M. Tsutsui, *Chem. Lett.*, 775 (1972).

"Sigma-Bonded Organometallic Compounds of Uranium (IV)" A. E. Gebala and M. Tsutsui, *J. Amer. Chem. Soc.*, **95**, 91-93 (1973).

"X-RAY Crystallographic Characterization of Uranium-Carbon Sigma Bond in Tricyclopentadienylthiophenyluranium(IV)", J. L. Atwood, C. F. Hains, Jr., M. Tsutsui and A. E. Gebala, *Chem. Comm.*, 452 (1973).

"Sigma-Bonded Organometallic Derivatives of the Lanthanides and Actinides", M. Tsutsui, N. Ely, and A. E. Gebala, *New York Acad. Sci., Ann.*, **239**, 160-170 (1974).

"Synthesis of a New Type of σ Bonded-Organouranium Compound: Mono and Bis-[tris (η^5 -cyclopentadienyl)uranium]ferrocene", M. Tsutsui and N. Ely, *J. Amer. Chem. Soc.*, **96**, 3650-3651 (1974).

"Organolanthanides and Organoactinides X: Synthesis of a New Type of σ -Bonded Organolanthanide Complex: (η^5 -C₅H₅)₂-Lu-C \equiv CPh", M. Tsutsui and N. Ely, *J. Amer. Chem. Soc.*, **96**, 4042 (1974).

"Organoactinides and Organolanthanides. XII. Bimetallic Tris(cyclopentadienyl)-uranium Derivatives with Uranium-Carbon σ Bonds", M. Tsutsui, N. Ely and A. Gebala, *Inorg. Chem.*, **14**, 78 (1975).

"Recent Development in Chemistry of Organolanthanides and Organoactinides", M. Tsutsui, C. Hyde, A. E. Gebala, and N. Ely. *Organotransition-Metal Chemistry*, Y. Ishii and M. Tsutsui (Ed.), Plenum Publishers, 93-108 (1975).

"New Lanthanide Alkyl and Aryl Derivatives of the Type (η^5 -C₅H₅)₂Lu-R", M. Tsutsui and N. Ely, *J. Amer. Chem. Soc.*, in press.

"An Unusual Type of Organolanthanide Complex Containing the Allyl Moiety: $(\eta^3\text{-C}_3\text{H}_5)_2\text{Lu-C}_3\text{H}_5$," M. Tsutsui and N. Ely, J. Amer. Chem. Soc., submitted.

"New Trends in Organic Derivatives of f-Elements", M. Tsutsui and N. Ely, Acc. of Chem. Res., submitted.

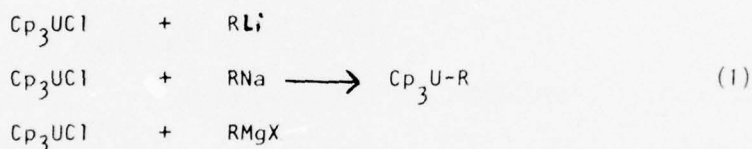
"Synthesis and Properties of New Sigma-Bonded Organolanthanide Complexes", M. Tsutsui and N. Ely, in preparation.

"Organolanthanides and Organoactinides Related to Catalysis", M. Tsutsui, Fin. Tech. Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major aim of this project was the synthesis and the characterization of organolanthanide and actinide compounds with new bonding modes. Of specific interest were species that contain a covalent bond(s) between the metal and organic moiety. The chemical and physical properties of these new compounds were explored.

New sigma-bonded species were prepared by the reaction of Cp_3UCl with either a lithium or sodium salt, or a Grignard reagent in ethereal solutions as shown in Scheme 1.



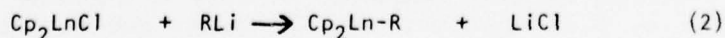
Where R = methyl, phenylacetylde, C_6H_5 , $\text{t-C}_4\text{H}_9$, acetylde, tolyl.

All of the complexes are extremely sensitive to oxygen and moisture, and many are pyrophoric. However, all of the compounds have remarkably high thermal stabilities. Nmr spectra of these complexes showed that the Cp protons appear as a sharp singlet at between 9 and 12 ppm upfield from benzene. The X-ray crystal structure for the phenylacetylde derivative clearly shows the U-C sigma bond.

Several unusual bimetallic complexes were synthesized: $\text{Cp}_3\text{U-ferrocene}$, $(\text{Cp}_3\text{U})_2\text{-ferrocene}$, and $(\text{Cp}_3\text{U})_2\text{-pphenyl}$. These are the only organoactinide complexes known which contain two $\text{Cp}_3\text{U-}$ moieties bound to the same ligand, and/or where the ligand is an organometallic moiety (ferrocene).

The magnetic susceptibility studies of these complexes have shown some very interesting and anomalous results. All three of these complexes display temperature dependent paramagnetism below 100°K.

A general method for preparing complexes containing lanthanide-carbon sigma bonds was developed. Using the reaction shown in Scheme 2, a number of alkyl, aryl, and alkynyl derivatives were synthesized.



The metals chosen vary from Gd to Yb. Like their uranium analogs, these new complexes are oxygen and moisture sensitive, but they are surprisingly thermally stable.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Structure and Properties of High Temperature Species
Related to Ablative Re-Entry and Solid Propellants
2. PRINCIPAL INVESTIGATOR: Dr. William Weltner, Jr.
Department of Chemistry
University of Florida
Gainesville, Florida 32611
3. INCLUSIVE DATES: 1 May 1968 - 31 October 1971
4. GRANT NUMBER: AFOSR-68-1588
5. COSTS AND FY SOURCE: \$80,000 FY 68; \$62,762 FY 70
\$64,564 FY 71
6. SENIOR RESEARCH PERSONNEL: Dr. W. T. Batchelder
Dr. J. M. Brom, Jr.
Dr. R. L. DeKock
Dr. W. C. Easley
Dr. L. B. Knight, Jr.
Dr. K. R. Thompson
7. JUNIOR RESEARCH PERSONNEL: Lon B. Knight
8. PUBLICATIONS:

"On Polytypism and Internal Rotation," W. Weltner, Jr., J. Chem. Phys. 52, 2469 (1969).

"ESR of the CN Radical in Inert Matrices," W. C. Easley and W. Weltner, Jr., J. Chem. Phys. 52, 197 (1970).

"ESR of the BC₂ Molecule in Inert Matrices at 4°K," W. Weltner, Jr. and W. C. Easley, J. Chem. Phys., 52, 1489 (1970).

"ESR Spectra of NO₂ in Inert Matrices," G. H. Myers, W. C. Easley and B. A. Zilles, J. Chem. Phys., 53, 1181 (1970).

"On the Spin-Doubling Constant Y, and g Tensor in ²Σ Molecules," L. B. Knight, Jr. and W. Weltner, Jr., J. Chem. Phys., 53, 4111 (1970).

"Hyperfine Interaction and Chemical Bonding in MgF, CaF, SrF, and BaF Molecules," L. B. Knight, Jr., W. C. Easley, W. Weltner, Jr. and M. Wilson, J. Chem. Phys., 54, 322 (1971).

"ESR of the BO Molecule in Inert Matrices: A Case of Extreme Preferential Orientation," L. B. Knight, Jr., W. C. Easley and W. Weltner, Jr., J. Chem. Phys., 54, 1610 (1971).

"Spectroscopy of the Rare-Earth Oxide Molecules in Inert Matrices," R. L. DeKock and W. Weltner, Jr., J. Phys. Chem., 75, 514 (1971).

"Spectroscopy of Carbon Molecules IV. C_4 , C_5 , C_6 , (and C_9)," K. R. Thompson, R. L. DeKock, and W. Weltner, Jr., J. Am. Chem. Soc., **93**, 4688 (1971).

"Hyperfine Interaction and Chemical Bonding in MgH , CaH , SrH , and BaH Molecules," L. B. Knight, Jr. and W. Weltner, Jr., J. Chem. Phys., **54**, 3875 (1971).

"Hyperfine Interaction, Chemical Bonding, and Isotope Effect in ZnH , CdH , and HgH Molecules," L. B. Knight, Jr. and W. Weltner, Jr., J. Chem. Phys., **55**, 2061 (1971).

" C_2O , CN_2 , and C_3O Molecules," R. L. DeKock and W. Weltner, Jr., (Accepted for publication in J. Am. Chem. Soc.).

"ESR and Optical Spectroscopy of the AlO Molecule at $4^{\circ}K$; Observation of an Al Complex and Its Interaction with Krypton," L. B. Knight, Jr. and W. Weltner, Jr., J. Chem. Phys., **55**, 5066 (1971).

"ESR of the PdH Molecule at $4^{\circ}K$," L. B. Knight, Jr. and W. Weltner, Jr., (J. Mol. Spectry.)

"Hyperfine Interaction and Chemical Bonding in the BeH Molecule," L. B. Knight, Jr., J. M. Brom, Jr., and W. Weltner, Jr., (J. Chem. Phys.)

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research has been devoted to the study of the optical and electron spin resonance (ESR) properties of so-called "high temperature" molecules.

These molecules are generally diatomic or small polyatomic species which are important contributors to flames, rocket exhausts, ablation products, and stellar atmospheres. Furthermore, they are of very basic interest in theoretical chemistry since the determination of their electronic and vibrational properties serves as a test of current calculations of such properties and contributes to the knowledge of chemical bonding. This is particularly true of the light diatomic hydride molecules such as BeH and MgH , where extensive ab initio calculations have been made which are severely tested by spin density measurements. These species have all been observed while trapped in the solid inert gases at temperatures near $4^{\circ}K$, i.e., using the matrix-isolation technique. The essentials of the research are as follows: Carbon Molecules and Their Oxides: Previous work on C_3 , C_2 , and C was extended to a study of C_4 , C_5 , C_6 and C_7 . These larger species are important in the vapor over graphite under extreme vaporization conditions. They were formed by diffusion and reaction of C , C_2 , and C_3 in solid argon at $\sim 12^{\circ}K$ and established as the observed species by ^{13}C substitution. Their Σ vibrational frequencies were determined and force constants calculated. C_2O and C_3O , formed by reaction of C atoms with CO , were also studied in the IR.

Boron Carbide Vapor: The BC_2 molecule was trapped and observed via ESR. The spin distribution in the $^2\Sigma$ ground state indicated that the odd electron is largely on boron so that the molecule is best depicted as $\cdot B = C = C \cdot$. BC , which theory showed to have a $^4\Sigma$ ground state, was not observed, apparently because of its low concentration.

Alkaline-Earth Diatomic Fluorides: ESR indicated that $\sim 4\%$ of the odd electron spin is on the fluorine atom in MgF and that it decreases down

the series MgF, CaF, SrF, BaF, as might be expected for increasing ionicity. The anisotropy of the hyperfine splitting on the metal indicated a highly distorted (polarized) M^+ ion in the field of the F^- ion. Crude wavefunctions could be calculated providing a rather definitive picture of these cases of almost classical ionic bonds.

Diatomic Hydrides: BeH, MgH, CaH, SrH, BaH, ZnH, CdH, HgH, and PdH molecules (all have $^2\Sigma$ ground states) were trapped and observed by ESR and optical spectroscopy. The spin densities in BeH and MgH could be compared with recent ab initio calculations of Davidson, et al, and serve as a sensitive indication of the accuracy of theory. The bonding in the heavier hydrides was examined relative to a united-atom model. Substitution of D for H in HgH caused a measurable shift in the spin distribution. The ground and excited state configurations for PdH were reassigned from these new spectroscopic data. A relation connecting the g tensor component with the spin-doubling constant, Y, observed in the gas phase, was derived and shown to be valid within about 10% over three orders of magnitude of Y.

Rare-Earth Oxide Molecules: All 14 solid rare-earth oxides were vaporized at temperatures near 2500°K. The monoxide and dioxide molecules and metal atoms in the vapor were trapped at 4°K and examined spectroscopically in the IR and visible regions. The vibrational frequencies of all of the monoxides lie between 808 and 832 cm^{-1} . Comparison was made with the meager gas phase data.

Solid Silicon Carbide and Polytypism: A theory was developed to explain the existence of the many polytypes of solid SiC and ZnS. It is based upon an analogy of the forces determining polytypism to those causing internal rotational barriers in molecules. The differing energies of the polytypes is then ascribed to the differing energies of "eclipsed" and "staggered" layers in the solids. Madelung constants for some of the prevalent polytype structures were calculated.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Analysis of the Collisional Redistribution of Molecular Energy in Gases
2. PRINCIPAL INVESTIGATOR: Dr. Lennard Wharton
James Franck Institute and
Department of Chemistry
University of Chicago
Chicago, Illinois 60637
3. INCLUSIVE DATES: 1 September 1971 to 30 November 1974
4. GRANT NUMBER: AFOSR-72-2176
5. COSTS AND FY SOURCE: \$49,574 FY 72; \$49,950 FY 73
\$45,067 FY 74
6. SENIOR RESEARCH PERSONNEL: Dr. P. Dehmer
Dr. D. Levy
Dr. R. Smalley
7. JUNIOR RESEARCH PERSONNEL: D. Auerbach
C. Becker
J. Cowen
B. L. Ramakrishna
K. Reed
L. Tsou
8. PUBLICATIONS:

"Absolute Total Cross Sections for Li-Molecule Scattering," L. Wharton, P. Dehmer and G. Ury, J. Chem. Phys. 58, 4724 (1973).

"High Resolution Differential Cross Section and Intermolecular Potentials: Li-Kr and Li-Xe," D. Auerbach, J. Chem. Phys. 60, 4116 (1974).

"Method for Increasing the Aperture of Space Focusing Lenses," L. Wharton, Rev. Sci. Instr. 45, 825 (1974).

"Velocity Dependence of Absolute Total Cross Sections for LiF Scattered by Non-Polar Targets," L. Wharton and P. Dehmer, J. Chem. Phys. 61, (1974).

"Target Density Dependence of Molecule-Molecule Absolute Total Scattering Cross Sections," L. Wharton and P. Dehmer, J. Chem. Phys. 61, (1974).

"Laser Spectroscopy of Supersonic Molecular Beams: Application to the NO₂ Spectrum," L. Wharton, R. E. Smalley, B. L. Ramakrishna and D. H. Levy, J. Chem. Phys. 61 (1974).

"Molecule-Atom High Resolution Differential Cross Sections and Rotational Transitions," Kent Reed (Manuscript in preparation).

"Atom-Atom and Atom-Molecule High Resolution Differential Cross Sections," D. Auerbach, C. Detz, K. Reed and L. Wharton (Manuscript in preparation).

"Electronic Spectrum of NO₂ Molecules," R. Smalley, D. H. Levy (Manuscript in preparation).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In the course of the present grant, investigation of elastic and inelastic phenomena were studied and applied in a number of different ways in order to contribute to our understanding of the collisional redistribution of molecular energy in gases. The studies included the following:

(1) Absolute total scattering cross sections of atoms and molecules. The variation of absolute total scattering cross section with relative velocity and target density were experimentally exploited and the interpretation advanced. Principal findings are the determination of absolute interatomic potentials, the determination of molecular electric quadrupole and dipolar scattering effects, and the demonstration of the great power of absolute cross sections in determining elastic and inelastic cross sectional effects.

(2) High resolution differential cross section studies of atoms and molecules. These are the highest resolution studies of differential cross sections and includes quantitative accuracy of the amplitude of the highest frequency oscillatory features. The data enabled quantitative inversion of intermolecular potentials. Principal findings are the "closure" of determination of intermolecular potentials by differential and total scattering cross sections. Interpretation is extended for molecule-atom cases to anisotropic terms in the molecule-atom potentials and hence translational-rotational energy exchange.

(3) Developments in state selection and supersonic beam technology to produce high intensity state selected beams for further detailed studies of rotational energy exchange. The principal finding is a means to produce rotationally state selected beams with as much beam intensity in a single state as was obtained previously in beams that had no state selection. This is currently being pursued experimentally for direct observation of rotational-translational differential cross sections.

(4) Exploitation of the collisional redistribution of rotational energy to assign the spectrum of the NO₂ molecule. In these studies the vibronic levels of NO₂ are identified by inspection, by the substantial elimination of rotational structure through cooling of NO₂ seeded into a supersonic argon beam. The electronic transitions were identified by high resolution (1 GHz) laser induced fluorescence. Principal findings are the explanation of the complexity of the NO₂ spectrum as a result of a massive pattern of perturbations and that the apparent rotational constants and spin-rotation constants are broadly distributed.

AFOSR Program Manager: J. T. Viola

Research Efforts (as of 30 September 1976)

(Alphabetical by Principal Investigator)

Reactions and Electrochemical Kinetics of Newly Generated Metal Surfaces	T. R. Beck Electrochemical Technology Corp. 3933 Leary Way, N. W. Seattle, Washington 98125
Chemical Transfer Lasers	David J. Benard Department of Physics University of California Santa Barbara, California 93106
Theoretical and Experimental Analysis of Alkaline Zinc Batteries	Douglas N. Bennion and John Newman Department of Chemical Engineering University of California Los Angeles, California 90024
Chemical Laser Studies of Chemical Reaction Dynamics	M. J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Spectroscopic & Kinetic Studies of Gas Phase Reactions	Herbert P. Broida Department of Physics University of California Santa Barbara, California 93106
Inelastic and Reactive Collisions of Translationally Excited Molecules	Philip R. Brooks Department of Chemistry Rice University Houston, Texas 77001
Electrochemistry of Hydrazine-Hydrazine Azide Mixtures	Charles T. Brown United Technologies Research Center United Technologies Corporation East Hartford, Connecticut 06108
Solid Electrode Studies Related to Corrosion Prevention, Fuel Cells and Batteries	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York, 14214
Energy Transfer and Chemical Reactions Important in Molecular Lasers	George Burns Department of Chemistry University of Toronto Toronto, Canada M5S 1A1
Kinetic Studies Involving Electronically-Excited Interhalogens and Halogens	M. A. A. Clyne Department of Chemistry Queen Mary College London E1 4NS, England
Novel Chemical Laser Systems	Terrill A. Cool School of Applied & Engineering Physics Cornell University Ithaca, New York 14850

Synthesis and Spectroscopic Investigation
of Inorganic Materials Possessing Unusual
Electronic Properties

Glenn A. Crosby
Department of Chemistry
Washington State University
Pullman, Washington 99163

Chemical Reactions that Produce Electronically
Excited Metal Atoms

David Davidovits
Department of Chemistry
Boston College
Chestnut Hill, Massachusetts 02167

Double Layer Structure and Electrode
Kinetics

Robert DeLevie
Department of Chemistry
Georgetown University
Washington, D.C., 20057

Sixth International Liquid Crystal Conference

A. DeVries and W. E. Bacon
Liquid Crystal Institute
Kent State University
Kent, Ohio 44242

Development of Practical MO Techniques for
Prediction of the Properties and Behavior
of Materials

Michael J. S. Dewar
Department of Chemistry
University of Texas
Austin, Texas 78712

The Role of the Polymer-Substrate Interphase
in Structural Adhesion

Lawrence T. Drzal
Research Institute
University of Dayton
Dayton, Ohio 45469

Evaluation of Chemical Research Relevant to
Current and Projected U. S. Air Force
Interests

Joseph E. Earley
Department of Chemistry
Georgetown University
Washington, D.C., 20007

Rates of Rapid Chemical Reactions

Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

One - and Two-Photon Optically Pumped Laser
Devices - New Chemical Laser Diagnostics and
Kinetic Probes

Robert W. Field
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

The Structure and Properties of Polymeric
Materials

Paul J. Flory
Department of Chemistry
Stanford University
Stanford, California 94305

Kinetic Spectroscopy of Metal Atom/Oxidizer
Chemiluminescent Reactions for Laser Applica-
tions

Arthur Fontijn
Aero Chem Research Laboratories, Inc.
Princeton, New Jersey 08540

Theoretical and Computational Studies of
Electronic Transitions in Molecular
Collisions

Thomas F. George
Department of Chemistry
University of Rochester
Rochester, New York 14627

Absolute Rate Constants for Combustion
Reactions Involving Free Radicals

D. M. Golden
Stanford Research Institute
Menlo Park, California 94025

Influence of Annealing of the Strengths of
Secondary Relaxations in Glasses

Martin Goldstein
Belfer Graduate School of Science
Yeshiva University
New York, New York 10033

Synthesis and Polymerization of Fluorobicyclobutanes to Chemically, Thermally and Dimensionally Stable Polymers

H. K. Hall, Jr.
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Photoluminescence Spectroscopy of Diatomic
Metal Oxides and Halides

David O. Harris
Department of Chemistry
University of California
Santa Barbara, California 93106

Proposed Program for the Determination of
DF and HF Rotational Relaxation Rates

J. J. Hinchey
United Technologies Research Center
United Technologies Corporation
East Hartford, Connecticut 06108

Mechanisms of Singlet Oxygen Generation by
Chemical Reaction

James K. Hurst
Department of Chemistry
Oregon Graduate Center
Beaverton, Oregon 97005

Solid State Materials Derived from Planar
Metal Complexes

L. V. Interrante and J. S. Kasper
General Electric Company
Research & Development Center
Schenectady, New York 12301

High Pressure Nuclear Magnetic Resonance
Relaxation Study of Supercritical Dense
Fluids

Jiri Jonas
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Effects of Structure on Physical Polymer
Interactions and Properties

F. E. Karasz
Polymer Science & Engineering
University of Massachusetts
Amherst, Massachusetts 01002

Computer Modeling of Pulsed Chemical
Lasers

Ronald L. Kerber
Department of Mechanical Engineering
Michigan State University
East Lansing, Michigan 48824

Novel Organophosphorus and Organonitrogen
Derivatives and their Use for the Synthesis
of Unusual Transition Metal Complexes

R. Bruce King
Department of Chemistry
University of Georgia
Athens, Georgia 30601

Theories of Energy Disposal in Chemical
Reactions

Aron Kuppermann
Division of Chemistry and
Chemical Engineering
California Institute of Technology
Pasadena, California 91109

Synthesis of Organofluorine Compounds
by Direct Fluorination

Richard Lagow
Department of Chemistry
Massachusetts Institute of
Technology
Cambridge, Massachusetts 02139

Synthesis of Organofluorine Compounds by
Direct Fluorination

Richard Lagow
Department of Chemistry
University of Texas
Austin, Texas 78712

Infrared Spectra of Fluid Films Under
Conditions of Incipient Bearing Failure

James L. Lauer
Applied Research Department
Sun Tech Inc.
Marcus Hook, Pennsylvania 19061

Energy & Chemical Change

R. D. Levine and John Deutch
Department of Chemistry
Massachusetts Institute of
Technology
Cambridge, Massachusetts 02139

Structure and Properties of Glasses

P. B. Macedo and T. A. Litovitz
Vitreous State Laboratory
Catholic University of America
Washington, D.C., 20017

Structure and Properties of Glasses

John D. Mackenzie
Department of Chemistry
University of California
Los Angeles, California 90024

Time-Temperature Studies of High Temperature
Deterioration Phenomena in Lubricant Systems -
Synthetic Ester Lubricants

L. R. Mahoney
Department of Chemistry
Ford Motor Company
Dearborn, Michigan 48121

Charge Transport Modes in Nickel Hydroxide
Electrodes

Joseph T. Maloy
Department of Chemistry
University of West Virginia
Morgantown, West Virginia 26506

Molecular Basis for Liquid Crystal Field
Effects

J. D. Margerum
Hughes Research Laboratories
Hughes Aircraft Corporation
Malibu, California 90265

Structure and Chemistry of Surfaces

Robert P. Merrill
School of Chemical Engineering
Cornell University
Ithaca, New York 14850

Calculation of Potential Energy Surfaces
and Collision Cross Sections

Harvey H. Michels
United Technologies Research Center
United Technologies Corporation
East Hartford, Connecticut 06108

The Relation Between the Chemical and Physical Structure and the Mechanical Response of Polymers

Ion Photofragment Spectroscopy - Potential Surfaces of Molecular Ions

Studies of Laser-Induced Photochemical Kinetics

Basic Studies Relating to the Synthesis of Unsymmetrical Dimethyl Hydrazine and Monomethyl Hydrazine by Chloramination

Gordon Research Conference on Glass

Electrochemistry of Solutes in Chloroaluminate Systems

Synthesis of Phosphatriazines for Potential High Temperature Fluids Applications

High Resolution Vacuum Ultraviolet Spectroscopy of Small Molecules

Chemical Lasers, Ultrarapid Scan Infrared Studies and Laser Induced Kinetic Processes

Poly(Fluoroorganophosphazene) Elastomers

Experimental and Theoretical Studies in Photochemistry

Molecular Beam Studies of Ionization Processes

Robert P. Morgan
McDonnell Douglas Research Labs
McDonnell Douglas Corporation
St. Louis, Missouri 63166

John T. Moseley and J. R. Peterson
Physical Sciences Division
Stanford Research Institute
Menlo Park, California 94025

R. A. McFarlane
School of Electrical Engineering
Cornell University
Ithaca, New York 14850

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K. A. Reynard and A. H. Gerber
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Cleveland, Ohio 44122

Stuart A. Rice
Department of Chemistry
University of Chicago
Chicago, Illinois 60637

Erhard W. Rothe
Department of Chemical Engineering
Wayne State University
Detroit, Michigan 48202

Organosilicon Compounds and Organosilicon Polymer Intermediates	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Molecular Energy Transfer by Collisional Processes Characteristic of Gas Lasers	Hyung Kyu Shin Department of Chemistry University of Nevada Reno, Nevada 89507
New Chemical Analysis Techniques	Robert E. Sievers Department of Chemistry University of Colorado Boulder, Colorado 80302
Basic Studies Relating to the Synthesis of Unsymmetrical Dimethyl Hydrazine and Monomethyl Hydrazine by Chloramination	Harry Sisler Department of Chemistry University of Florida Gainesville, Florida 32611
Reactive Atomic Species Generated at High Temperature and their Low Temperature Reactions to Form Novel Substances	P. S. Skell Department of Chemistry Pennsylvania State University University Park, Pennsylvania 16802
Effects of Oxygen and Water Vapor on the Compressive Strength of Boundary Films on Iron Crystals	D. Snediker Department of Tribomechanics Battelle Memorial Institute Columbus, Ohio 43201
Isomeric Graft Copolymers and Interpenetrating Polymer Network Structures	L. H. Sperling Department of Chemical Engineering Lehigh University Bethlehem, Pennsylvania 18015
Formation and Deactivation Processes in Electronic Transition, Chemically Pumped Lasers	J. I. Steinfeld and J. L. Gole Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Third Summer Workshop on Electronic Transition Lasers	J. I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Transition Metal Compounds with Potential Electronic and Radiation Resistant Properties	F. G. A. Stone Department of Chemistry University of Bristol Bristol BS8 ITS, England
Molecular Beam Studies of Collisional Excitation and Energy Exchange in Polyatomic Molecules	R. B. Subbarao and J. B. Fenn Department of Engineering Sciences Yale University New Haven, Connecticut 06520
Collisional Excitation and Ionization	Thomas O. Tiernan Department of Chemistry Wright State University Dayton, Ohio 45431

New Perfluoropolymer-Forming Reactions

M. S. Toy
Science Application, Inc.
Sunnyvale, California 94086

Measurement of IR Signatures of Molecular
Species from Advanced Rocket Propellants

C. E. Treanor and Anthony Russo
CALSPAN Corporation
Buffalo, New York 14221

Structural and Dynamic Studies of Materials
Possessing High Energy Content

Nicholas J. Turro
Department of Chemistry
Columbia University
New York, New York 10027

Applied Quantum Chemistry of Nonmetallic
Materials

John T. VanWazer
Department of Chemistry
Vanderbilt University
Nashville, Tennessee 37203

Unsaturated Organosilicon Heterocycles

W. P. Weber
Department of Chemistry
University of Southern California
Santa Barbara, California 93106

High Temperature Molecules and Molecular
Energy Storage

William Weltner, Jr.
Department of Chemistry
University of Florida
Gainesville, Florida 32611

Chemical Reactions and Properties of Organo-
silicon Compounds Related to New Materials

Robert C. West
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Studies of Rotationally Cooled Molecules in
Molecular Beams by Laser Spectroscopic
Techniques

Lennard Wharton
Department of Chemistry
University of Chicago
Chicago, Illinois 60637

Energies and Conformations of Molecules

K. B. Wiberg
Department of Chemistry
Yale University
New Haven, Connecticut 06520

Chemical Kinetics of Metal Atom Reactions in
the Gas Phase

John Wiesenfeld
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Cornell University
Ithaca, New York 14853

Analytical Gas Phase Spectrometry and
Combustion Diagnostics

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X-Ray Photoelectron Spectroscopic Studies
of Electrode Surfaces

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Internal State Identification of Reaction
Products

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Completed Project Summaries FY76 and 77

Alphabetical by Principal Investigator

Visible Wavelength Chemiluminescence Initiated by CO ₂ Laser Radiation	Simon H. Bauer Professor of Chemistry Cornell University Ithaca, New York 14853
Molecular Electronic Photodissociation Laser Studies	Dr. Michael J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Chemical Laser Studies of Chemical Reaction Dynamics	Dr. Michael J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Spectroscopy in Kinetic Studies of Gas- Phase Reactions	H. P. Broida University of California Department of Physics Santa Barbara, California
Kinetics of Association-Dissociation Reactions and Energy Transfer in Diatomic Molecules	Dr. George Burns Department of Chemistry Lash Miller Chemical Laboratory University of Toronto 80 St. George Street Toronto, Ontario Canada, M5S 1A1
Luminescent Transition Metal Complexes in Magnetic and Electric Fields	Professor G. A. Crosby Department of Chemistry Washington State University Pullman, Washington 99163
Energy Migration Involving Irradiated Solids	Joseph Cunningham University College Cork Ireland
Chemical Reactivity and Molecular Beams Scattering	J. B. Fenn Department of Engineering and Applied Science Yale University New Haven, Connecticut
Ionization Processes Relevant to the Formation of New Materials	Professor Harlan L. Goering Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
The Absolute Measurement of Rate Constants for Some Key Reactions Involving Free Radicals	Dr. David M. Golden Stanford Research Institute Menlo Park, California 94025
Effect of Structure on Physical Properties of Polymers	Dr. Frank E. Karasz Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002

Infrared Spectra of Fluid Films under Con-
ditions of Incipient Bearing Failure, Phase I

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Sun Oil Company
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AFOSR Program at UCLA in the Chemistry of
Materials Under Extreme Environmental
Conditions

Dr. Willard F. Libby
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Los Angeles, California

Structure and Properties of Glasses

Dr. P. B. Macedo and
Dr. T. A. Litovitz
Vitreous State Laboratory
Catholic University of America
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Molecular Basis for Liquid Crystal Field
Effects

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The Reactivity and Structure of Solid
Surfaces

Dr. Robert P. Merrill
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Electrochemical Studies in Aluminum
Chloride Melts

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Experimental and Theoretical Studies in
Photochemistry

Stuart A. Rice
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High Energy Chemical Reactivity

John Root
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Highly Halogenated Organic and
Organometallic Materials and Strained
Ring Organometallics

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Photochemical Addition of Benzene to
Unsaturated Materials

Dr. R. Srinivasan
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Second Summer Colloquium on Electronic
Transition Lasers

Dr. J. I. Steinfeld
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Massachusetts Institute of
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The Chemical Kinetics of Some Elementary
Reactions of Oxygen Atoms

Dr. Richard B. Timmons
Department of Chemistry
Catholic University
Washington, D.C.

Gas Phase Spectrometry Methods - Trace
Analysis of Elements and Analytical Gas
Phase Spectrometry and Combustion
Diagnostics

Dr. James D. Winefordner
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Electrode Mechanisms Using Reflection
and Electron Spectroscopy

Professor Nicholas Winograd
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Completed Project Summaries

FY76 and 7T

COMPLETED PROJECT SUMMARY

1. TITLE: Visible Wavelength Chemiluminescence Initiated by CO₂ Laser Radiation.
2. PRINCIPAL INVESTIGATOR: Simon H. Bauer
Professor of Chemistry
Cornell University
Ithaca, New York 14853
3. INCLUSIVE DATES: 1 February 1974 - 29 February 1976.
4. GRANT NUMBER: AFOSR-74-2629.
5. COSTS AND FY SOURCE: \$30,000 FY74; \$31,000 FY75
6. SENIOR RESEARCH PERSONNEL: Dr. E. Bar-Ziv
Dr. E. Kamaratos
Dr. E. Lory
7. PUBLICATIONS:

"Visible Wavelength Chemiluminescence Initiated by CO₂ Laser Radiation", S. H. Bauer and E. Bar-Ziv, Final Tech Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to find experimental conditions for generating high intensity chemiluminescence in the visible and ultraviolet regions of the spectrum by reacting, in the gas phase, metal atoms with oxidizers, such as the halogens, oxygen, nitrogen or sulfur, incorporated in molecules wherein they are weakly bound; and to investigate the chemical kinetics that control the production of chemiluminescence. The ultimate objective is to find combinations of reagents and operating conditions wherein inverted electronic state populations are generated, suitable for developing lasers.

Studies of chemiluminescence in the visible, emitted during highly exothermic reactions between metal atoms and oxidizers, have been underway for several years in this laboratory and in many other places in the country. In selecting suitable mixtures several essential criteria should be kept in mind: (1) the systems studied should be scalable; (2) they should be inherently capable of producing high powers; (3) they could be either cw or pulsed, but if the latter the pulse length should be in the microsecond regime rather than nanoseconds. As yet no diatom metal-oxidizer laser has been discovered for the visible, although infrared lasers have been demonstrated (Rice, et.al., Appl. Phys. Lett., 28, 444 (1976)). The initial thrust for the visible region was based on an extrapolation of the successful development of chemical lasers in the infrared. The major difference between the infrared program and the thus far unsuccessful quest in the visible, is that the first depends on a non-Boltzmann partition of exothermicity among vibrations in the ground electronic state, while the latter requires substantial channeling of the available energy into excited electronic states. As anticipated, and experimentally confirmed, stricter symmetry requirements are imposed on the nature of the reaction. Also, there is a crucial experimental restriction --- the relative shortness of the spontaneous radiative lifetime of the excited states compared with the mixing time that can be achieved in conventional flow reactors. In the infrared the corresponding critical ratio is the collisional lifetime relative to the mixing time, and this can be made greater than unity by control of reagent pressures.

The proposed solutions were of two kinds. In one configuration supersonic mixing was used, in the other, the components are premixed. Thus, the carriers of the metal atom and the oxidizer must be mutually compatible; then one rapidly initiates the exoergic reactions. Specific designs clearly depend on the branching ratios for the production of excited vs ground state populations.

In this research, the second program was followed working with premixed gases, and initiating the reaction with a pulse of CO₂ laser radiation. Mixtures of encapsulated metal vapors, SF₆, and an oxidizer were subjected to a 20J, 1 microsecond pulse of a CO₂ laser. The SF₆ acts as an energy absorber and transfer agent for rapidly raising the temperature of the mixture to 1500-2000°K. This sets off a reaction which rapidly strips the ligands from the central metal atom and develops a premixed metal-oxidizer system for further reaction. This procedure has the attractive feature that the initiation step is not so vigorous as to disrupt excessively the oxidizer species. After the metal oxidation is initiated, the consequent temperatures developed are very high. For some combinations very large luminosities were recorded. It was estimated that as many as one photon for every ten metal atoms present were generated under some conditions. The specific systems tested and the techniques developed during this program are described in the final report. Systems included: SiH₄, SF₆, N₂O; Sn(CH₃)₄, SF₆, N₂O; Pb(CH₃)₄, SF₆, NO; and Bi(CH₃)₃, SF₆, NO.

AFOSR Program Manager: J. T. Viola, Lt Colonel

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Electronic Photodissociation Laser Studies
2. PRINCIPAL INVESTIGATOR: Dr. Michael J. Berry
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706
3. INCLUSIVE DATES: 1 February 1974 - 31 January 1976
4. GRANT NUMBER: AFOSR-74-2666
5. COSTS AND FY SOURCE: \$44,912 FY74
\$41,954 FY75
6. SENIOR RESEARCH PERSONNEL: Dr. O. Kafri
Dr. J. T. Knudtson
7. JUNIOR RESEARCH PERSONNEL: S. T. Aminoto
S. N. Bittenson
R. L. Gaither
R. J. Gill
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S. K. Liu
K. V. Reddy
G. A. West

8. PUBLICATIONS:

"Vibronic Surprisal Analysis of the Dynamics of Photodissociation and Related Reactions," M. J. Berry, Chem. Phys. Letters, 29, 323 (1974).

"Golden Rule Calculation of Product Vibronic Population Inversions in Photodissociation and Related Reactions," M. J. Berry, Chem. Phys. Letters, 29, 329 (1974).

"Cyanide Radical Molecular Electronic Laser: Grating Selection Determination of Population Inversions," J. T. Knudtson and M. J. Berry, in J. I. Steinfeld (editor), Electronic Transition Lasers (MIT Press, Cambridge, Mass., 1976).

"Methyl Isocyanide Photodissociation: Chemical Laser Determination of Energy Partitioning into the Cyanide Radical Photochemical Product," J. T. Knudtson and M. J. Berry, to be submitted to J. Chem. Phys.

"Molecular Electronic Photodissociation Laser Studies," M. J. Berry, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main objectives of this work were to identify photochemical reactions suitable for production of electronic chemical lasers and to determine reaction and relaxation rate parameters for promising candidates. Extensions to bimolecular reaction examples were made as the work progressed.

Grating-tuned pulsed chemical lasers were operated on several reaction systems (the CH_3NC photodissociation electronic chemical laser, the $\text{F} + \text{HI}(\text{DI})$ bimolecular chemical lasers, etc) in order to study features of energy partitioning and collisional energy redistribution. In photodissociation of CH_3NC at $\lambda > 1550 \text{ \AA}$, measurements of the relative gains of lasing transitions showed that $\text{CN}^*(\text{A}^2\pi, v = 0)$ is the predominant nascent photochemical product (>80%) and that spin-orbit and rotational relaxation are rapid processes on present chemical laser emission timescales. Relative gains of lasing HF and DF transitions were measured in the $\text{F} + \text{HI}$, HBr , HCl and $\text{F} + \text{DI}$, DBr , DCI chemical laser systems; vibronic population inversions were determined from these gain measurements. Curved surprisal plots in the $\text{F} + \text{HI}$ and $\text{F} + \text{DI}$ systems indicate that electronically excited iodine atoms may be formed chemically with moderate efficiency.

New types of chemical laser apparatus were constructed: a) a sub-microsecond flash photolysis concentric lamp array and b) a MgF_2 -windowed coaxial flashlamp for photolysis down to ca. 1200 \AA . Both devices, together with conventional chemical laser equipment, were used to search for new electronic chemical lasers based upon photochemical and bimolecular reactions; no new lasers were discovered.

Support and screening experiments involving VUV spectroscopy and fluorescence quantum yield determinations were completed at the University of Wisconsin Synchrotron Radiation Facility. Electronically excited cyanide radicals ($\text{CN}^*(\text{B}^2\Sigma^+)$ and $\text{CN}^*(\text{A}^2\pi)$) were found to be major products in photodissociation and predissociation of HCN , $(\text{CN})_2$, cyanogen halides, and other cyanide parents.

Certain theoretical work was performed to determine dynamical features that govern vibronic population distributions in photochemical reactions. Information theoretic analyses and computations based upon a Franck-Condon model of introfragment dynamics showed that the structural change of a diatomic fragment in evolving from reactant to photochemical product is the dominant factor that produces observed vibronic state distributions. Analyses of related reaction examples (collisional dissociative excitation and electronis-to-vibrational energy transfer) were also carried out.

AFOSR Program Manager: Lt Col J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Laser Studies of Chemical Reaction Dynamics
2. PRINCIPAL INVESTIGATOR: Dr. Michael J. Berry
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706
3. INCLUSIVE DATES: 1 September 1972 - 31 August 1976
4. GRANT NUMBER: AFOSR-73-2423
5. COSTS AND FY SOURCE: \$ 40,953 FY73
\$ 38,574 FY74
\$ 55,671 FY75
\$100,131 FY76
6. SENIOR RESEARCH PERSONNEL: Dr. R. G. Bray
Dr. O. Kafri
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7. JUNIOR RESEARCH PERSONNEL: S. T. Animoto
S. N. Bittenson
B. D. Cannon
J. C. Elward
R. J. Gill
W. Henke
D. E. Klimek
S. K. Liu
K. V. Reddy
W. A. Tricomi
G. A. West

8. PUBLICATIONS:

"The F + H₂, D₂, HD Reactions: Chemical Laser Determination of the Product Vibrational State Populations and the F + HD Intramolecular Kinetic Isotope Effect," M. J. Berry, J. Chem. Phys., 59, 6229 (1973).

"Hot-Atom Initiated Chemical Laser Study of the H* + SF₆ Reaction," M. J. Berry, Chem. Phys. Letters, 22, 507 (1973).

"Golden Rule Calculation of Reaction Product Vibronic State Distributions," M. J. Berry, Chem. Phys. Letters, 27, 73 (1974).

"The Chloroethylene Photochemical Lasers: Vibrational Energy Content of the HCl Molecular Elimination Products," M. J. Berry, J. Chem. Phys., 61, 3114 (1974).

"CN Photodissociation and Predissociation Chemical Lasers: Molecular Electronic and Vibrational Laser Emissions," G. A. West and M. J. Berry, J. Chem. Phys., 61, 4700 (1974).

"Analysis of Electronically Nonadiabatic Chemical Reactions: An Information Theoretic Approach," U. Dinur, R. Kosloff, R. D. Levine, and M. J. Berry, Chem. Phys. Letters, **34**, 199 (1975).

"Laser Studies of Gas-Phase Chemical Reaction Dynamics," M. J. Berry, Ann. Rev. Phys. Chem., **26**, 259 (1975).

"Suggestion for a New Two-Photon Cross Section," O. Kafri, Chem. Phys. Letters, **36**, 624 (1975).

"Chemical Laser Studies of Energy Partitioning Into Chemical Reaction Products," M. J. Berry, in R. D. Levine and J. Jortner (editors), Molecular Energy Transfer (Wiley, New York, 1976).

"A Polyatomic Chemical Laser: Vibrationally Excited Hydrogen Cyanide Produced by the $CN + H_2$ Bimolecular Reaction," G. A. West and M. J. Berry, Opt. Comm., **18**, 128 (1976).

"A New Empirical Potential Hypersurface for Bimolecular Reaction Systems," O. Kafri and M. J. Berry, Faraday Disc. Chem. Soc., **62**, XXX (1976).

"An Intracavity Dye Laser Technique for Spectroscopic and Kinetic Measurements of Transients," R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry, to be published in J. I. Steinfeld (editor), Electronic Transition Lasers, Vol 2 (MIT Press, Cambridge, MA, 1977).

"Measurement of Highly Forbidden Optical Transitions by Intracavity cw Dye Laser Spectroscopy," R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry, submitted to Chem. Phys. Letters.

"Chemical Laser Studies of Chemical Reaction Dynamics," M. J. Berry, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The central emphasis of this project has been the study of molecular reaction dynamics (i.e., the study of rate processes on a reactant state to product state level of inquiry) for elementary bimolecular, unimolecular, and photochemical reactions. Some practical consequences of the work include the discovery of several new chemical lasers and the determination of important rate processes that affect the operation and performance optimization of numerous chemical laser systems.

In the discovery category, the most interesting systems are the cyanide radical molecular electronic lasers (produced by photodissociation and predissociation of CH_3NC , $(CN)_2$, HCN , and other cyanide parents; CN lases in red band transitions ($A^2\pi_i - X^2\sigma^+$) between 1.1 - 2.0 μ), haloalkane photoelimination lasers (e.g., $CH_3 \xrightarrow{h\nu} HCl^+ + CH_2 = CHCl$; HCl lases in vibration-rotation transitions of $v = 1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 2$, and $4 \rightarrow 3$ bands between 3.5 - 4.2 μ), a "hot-atom" initiated laser (produced by impact of translationally "hot" hydrogen atoms on SF_6 with subsequent reaction of collisionally dissociated fluorine atoms with HI; the HF product of the $F + HI$ reaction lases in vibration-rotation transitions of $v = 1 \rightarrow 0$ through $v = 5 \rightarrow 4$ bands between 2.5- 3.3 μ), and the hydrogen cyanide polyatomic chemical laser (produced by the bimolecular reaction $CN + H_2 \rightarrow HCN^+ + H$; NCN lases in vibration-rotation transitions of the $00^01 \rightarrow 00^00$, $00^01 \rightarrow 01^10$, and $10^01 \rightarrow 10^00$ bands between 3.0 \rightarrow 3.9 μ).

Detailed measurements of energy partitioning into reaction products in the above and other chemical laser systems were made possible by the development of a new technique (grating-tuned operation of chemical lasers and measurement of the relative optical gains of lasing transitions). Complete HX(DX) product vibronic state distributions were obtained for the $F + H_2$, D_2 , HD bimolecular reactions, for many photochemical reactions (e.g., $CH_2 = CCl_2 \xrightarrow{h\nu} HCl + HC = CD$), and for unimolecular reactions (e.g., $CHF_3 \rightarrow HF + CF_2$). Other quantitative kinetic information (e.g., on kinetic isotope effects in the $F + HD$ reaction) was also obtained by chemical laser methods.

Two main classes of support experiments were carried out: a) vacuum ultraviolet (VUV) absorption spectroscopy and fluorescence excitation using a synchrotron radiation source with on-line computer control, data acquisition, and signal processing, and b) tunable intracavity cw dye laser quenching spectroscopy. VUV absorption spectra, extinction coefficient, and assignments were obtained for interesting photochemical reactants such as $HFCO$, $CH_2 = CHCl$, and HCN . In addition, fluorescence excitation spectra and quantum yields for photochemical reactants and products were measured. Dye laser quenching spectroscopy was used to detect extremely low-intensity transitions such as the 5th overtone band ($v' = 6 \leftarrow v'' = 0$) of HCl in the visible spectral region. Applications of dye laser quenching spectroscopy to the discovery of transient optical gains in potential electronic lasers were initiated.

Certain theoretical approaches toward reaction dynamics were also pursued. A simple dynamical model which predicts product vibronic state distributions was devised and successfully applied to reaction and energy transfer systems. Ab initio molecular electronic structure and potential hypersurface computations were performed for some chemical laser reaction systems. Information theoretic methods were used to analyze dynamical features of bimolecular and photochemical reactions and to predict electronic branching ratios for potential bimolecular electronic chemical lasers. Finally, a new empirical procedure for the construction of potential energy hypersurfaces for bimolecular chemical reactions was devised; initial quasiclassical trajectory computations using the empirical surfaces have been performed.

AFOSR Program Manager: Lt Col J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Spectroscopy in Kinetic Studies of Gas-Phase Reactions

2. PRINCIPAL INVESTIGATOR: H. P. Broida
University of California
Department of Physics
Santa Barbara, California

3. INCLUSIVE DATES: 1 May 1974 - 31 August 1976

4. GRANT NUMBER: AFOSR- 74-2724

5. COSTS AND FY SOURCE: \$29,358 FY74; \$54,353 FY75; \$64,062 FY76

6. RESEARCH PERSONNEL:

J. M. Brom, Jr.	R. W. Field
M. M. Hessel	G. A. Capelle
R. E. Drullinger	M. A. Revelli
S. Rosenwaks	J. C. Wyss
R. E. Steele	C. Linton
D. J. Benard	R. S. Bradford, Jr.

7. PUBLICATIONS:

"Photodissociative Production of $O(^1S)$ and $N(^2D)$ from N_2O in an Argon Matrix at 4K", J. M. Brom, Jr., H. P. Broida, Chem. Phys. Lett. **33**, 384 (1975).

"Chemiluminescent Reactions in a Heat Pipe Oven", M. M. Hessel, R. E. Drullinger, H. P. Broida, J. Appl. Phys. **46**, 2317 (1975).

"Chemiluminescence of AlO ", S. Rosenwaks, R. E. Steele, H. P. Broida, J. Chem. Phys. **63**, 1963 (1975).

"Laser Photoluminescence of TiO in Ne at 4 K", J. M. Brom, Jr., H. P. Broida, J. Chem. Phys. **63**, 3718 (1975).

"CW Chemical Laser Gain at 10.6 Microns", D. J. Benard, Chem. Phys. Lett. **35**, 167 (1975).

"Optical-Optical Double Resonance Laser Spectroscopy of BaO ", R. W. Field, G. A. Capelle, M. A. Revelli, J. Chem. Phys. **63**, 3228 (1975).

"CW Chemical Transfer CO_2 Laser" D. J. Benard, Appl. Phys. Lett. **27**, 542 (1975).

"Chemiexcitation Transfer to High Lying Rydberg Levels of Al" S. Rosenwaks, H.P. Broida, J. Opt. Soc. Am. **66**, 76 (1976).

"Observation of a triplet $\pi - X$ singlet sigma Intercombination Emission in AlF ", S. Rosenwaks, R. E. Steele, H. P. Broida, Chem. Phys. Lett. **38**, 121 (1976).

"Vibrational Analysis of the A' singlet π State of Barium Oxide Using Two Isotopes" J. C. Wyss, H. P. Broida, J. Mol. Spectros. **59**, 235 (1976).

"Chemiluminescent Spectra of PbO from Reactions of Pb Atoms", C. Linton, H. P. Broida, J. Mol. Spectros. **62**, 396 (1976).

"Photoluminescence, Lifetimes, and Discharge Excitation of Cu_2 ", R. E. Steele, J. Mol. Spectros. **61**, 477 (1976).

"Chemiluminescent Reactions of Al Atoms and Halogens" S. Rosenwaks, J. Chem. Phys. **3668** (1976).

"Flame Spectroscopy of TiO: I. Chemiluminescence" C. Linton, H. P. Broida, J. Mol. Spectros. xx, (in press 1976).

"Flame Spectroscopy of TiO: II. Photoluminescence of the $a(C^3\Delta - X^3\Delta)$ System", C. Linton, H. P. Broida, J. Mol. Spectros. xx, (in press 1976).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Various diatomic molecular species have been produced in vacuum flow systems; typically metal vapor entrained in an inert gas is reacted with a halogen or oxidant. These exothermic reactions produce product molecules in excited states whose fluorescence (chemiluminescence) is analyzed. Laser induced fluorescence (photoluminescence) is also used to probe both ground and excited electronic states.

The following research summary is organized according to experimental techniques:

Chemiluminescence, Photon Yields and Branching Ratios: Reactions of lead with N_2O , O , O_2 , and O_3 were investigated under a wide variety of conditions and were found to depend dramatically upon both oxidant species and pressure. Many new bands were found and molecular constants were determined.

Modifications to the standard furnace system allowed extension of its upper temperature limit by several hundred degrees, to 2100 K, and permitted production of TiO. O_2 , N_2O , NO and CO_2 were used as oxidants of the titanium atoms. Ti + O_2 flames had electronic and vibrational temperatures of 2500 ± 500 K while Ti + N_2O flames were approximately twice as hot, and exhibited wider departures from Boltzmann statistics. Ultraviolet emission was three orders of magnitude higher with N_2O than with O_2 .

Preliminary photon yield data have been taken for the reactions of copper with F_2 , NF_3 and SF_6 . Chemiluminescence spectra of CuF have been taken in the 200-1100 nm region and corrected by computer for relative spectral response of the detection system. Three new electronic states have been discovered with transitions at 438, 568 and 680nm. Total photon yields from 200-800nm were less than 0.5% for the reaction $Cu + F_2$, and lower for $Cu + NF_3$; 60-90% of the emission was in the A-X transition, and 10-40% divided between the B-X and C-X systems.

Aluminum atoms diluted in a buffer gas were reacted with F_2 , Cl_2 , Br_2 , I_2 , NF_3 , and SF_6 to produce diatomic aluminum halides in chemiluminescent flames. Emission from a triplet pi to X singlet sigma was observed for all the halides, and for Al, AlF and AlCl, higher electronic states were also observed. Photon yields were 2% for $Al + NF_3$, and less than 0.01% for the other reactants. In the case of $Al + NF_3$, about 90% of the total yield was due to Al atomic emission and in fact the atomic emission extended up to the ionization limit at 207nm. Energy transfer from metastable molecules was invoked as the excitation mechanism.

Observation of intercombination emission from AlF allowed the first direct determination of the a triplet pi to X singlet sigma separation, which agreed well with an earlier value calculated from vibrational perturbations observed in the A singlet pi state.

Emission from ultraviolet to near infrared was observed from flames of Al atoms reacting with various oxidants. Photon yields for the reactions varied widely from 3% for $Al +$ microwave discharged O_2 , and 2% for O_3 , to 0.4% for N_2O and less than 0.005% for all other oxidants. The A doublet pi to X doublet sigma system, which had not previously been observed in emission, was seen with several of the oxidants.

PHOTOLUMINESCENCE: A single mode tunable dye laser was used to induce photoluminescence from CuF. High resolution scans near the origin of the A singlet $\pi - X$ singlet sigma transition show strong perturbations from a newly discovered state of around 17600 cm^{-1} .

Laser induced photoluminescence has been observed from TiO molecules produced in a chemiluminescent flame of $\text{Ti} + \text{O}_2$. Ar⁺ and cw dye lasers were used in a detailed study of the alpha (C triplet delta - X triplet delta) system in emission. Techniques were developed for assigning photoluminescence transitions involving states of high multiplicity in molecules with several isotopes.

LIFETIME MEASUREMENTS: The radiative lifetimes have been measured for the A singlet π , B singlet sigma and C singlet π states of CuF and have been found to be .5, .7_x and 12 microseconds respectively. Tunable pulsed dye lasers were used for the measurements with either flashlamp (1 microsec duration) or nitrogen laser (1 nsec pulse duration) excitation. A computerized detection system was developed to enable signal averaged and wavelength scanned lifetime measurements to be made.

Radiative lifetimes have been measured for the A and B states of Cu₂. Using a N₂-pumped tunable dye laser, lifetimes of 30 ± 15 nsec at a background argon pressure of .5 torr and 20 ± 15 nsec at 10 torr were measured for the first three vibrational levels of the B state. The A state lifetime of the V=0 level is 70 ± 15 nsec at .5 torr and 50 ± 15 nsec at 10 torr.

COMPUTER ANALYSIS: In studies of the CuF, A singlet π state, comparison of data to synthetic spectra revealed the necessity of using different B values for the Q vs the P and R branches to obtain suitable agreement, and thereby revealed the existence of a new state which was responsible through perturbations for the anomalies in the A singlet π state.

Such comparison of synthetic and observed spectra also facilitates determination of rotational and vibrational temperatures in chemiluminescent flames.

EXCITATION TRANSFER: Combustion of Mg vapor in N₂O with He and CO₂ diluents in a low-loss laser cavity resulted in cw oscillation at 10.6 microns. The pumping takes place via chemical reaction and subsequent electronic-vibrational (E-V) energy transfer. The first step, whose exothermicity ultimately drives the laser, is the formation of electronically excited MgO. A large proportion of this MgO is in states whose radiative decay is slow. In the presence of CO₂ the dominant mode of destruction of these metastable MgO molecules is believed to be collisional conversion of their electronic excitation to vibrational excitation of CO₂, with the consequent inversion of the (001) level with respect to the (100) level.

High-lying Rydberg levels of Al were excited in a chemical reaction with NF₃. A possible mechanism is that high lying levels of Al are populated by energy transfer from excited molecular nitrogen produced in the Al + NF₃ mixture. Al atomic states up to the series limit were observed with NF₃ as well as in another experiment with microwave discharge N₂. While with active nitrogen, the resulting populations of the Al excited states followed a Boltzmann distribution at about 3000 K, in the case of the NF₃ the population distribution was non-Boltzmann and skewed toward higher energies.

Active nitrogen was also used in experiments on TiO and PbO flames, where it materially enhanced the molecular emission as well as causing intense atomic emission from the metal. In the case of Pb the effect was primarily to increase the electronic temperature while maintaining a Boltzmann distribution. It is believed that PbO was produced by transfer from active nitrogen to PbO. Similar explanations apply in the case of TiO.

GAIN MEASUREMENTS: Intracavity laser gain measurements using a CO_2 electrical discharge probe laser were made to study flames of Ba, Ca and Mg burning in a mixture of N_2O , CO_2 and He. Gain at 10.6 microns was detected for each of these metals. For²the Mg flames the gain coefficient was found to be in the range of $10^{-3} - 10^{-2}/\text{cm}$. The addition of N_2 diluent enhanced the gain, whereas CO diluent quenched it. These measurements led to the observation of cw lasing.

AFOSR Program Manager: Lt Col J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Kinetics of Association-Dissociation Reactions and Energy Transfer in Diatomic Molecules.

2. PRINCIPAL INVESTIGATOR: Dr. George Burns
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3. INCLUSIVE DATES: 1 September 1973 - 31 August 1975

4. GRANT NUMBER: AFOSR-74-2620

5. COST AND FY SOURCE: \$23,000 FY74

6. SENIOR RESEARCH PERSONNEL:

Dr. H. W. Chang	Dr. C. W. Wilson
Dr. R. D. Coombe	Dr. W. H. Wong
Dr. D. T. Chang	

7. JUNIOR RESEARCH PERSONNEL:

J. D. Brown
R. G. MacDonald

8. PUBLICATIONS:

"Potential Energy Surface for the Hydrogen Molecule-Helium System", C. W. Wilson, Jr., R. Kapral and George Burns, Chem. Phys. Ltrs., 23, 448 (1974).

"Trajectory Studies of Atomic Recombination Reactions. VI. Recombination of Oxygen Atoms in Argon", W. H. Wong and G. Burns, Can. J. Chem., 52, 1988 (1974).

"The Thermal Emission of Iodine", J. D. Brown and George Burns, Canadian Journal of Physics, 52, 1862 (1974).

"Dynamics of Collisional Dissociation: I_2 in Ar and Xe", W. H. Wong and George Burns, Proc. Roy. Soc. London, A341, 105 (1974).

"Study of Atomic Recombination Over a Wide Pressure Range", George Burns and W. H. Wong, J. Am. Soc., 97, 710 (1975).

"The Dynamics of Dissociation of Diatomic Molecules and Mass Effect", W. H. Wong and George Burns, J. Chem. Phys., 62, 1712 (1975).

"Recombination of Iodine Atoms by Flash Photolysis over a Wide Temperature Range. VI. I_2 in HCl, HBr and SO_2 ", H. W. Chang and George Burns, J. Chem. Phys., 62, 2426 (1975).

"Recombination of Bromine Atoms Between 300 and 6000°K, Theory and Experiment", R. K. Boyd, George Burns, D. T. Chang, R. G. MacDonald and W. H. Wong, Fifteenth Symp. (Intern.) Combust., p. 731, The Combustion Institute (1975).

"Kinetics of Association-Dissociation Reactions and Energy Transfer in Diatomic Molecules", George Burns, Fin Tech. Rpt.,

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In this project, the recombination-dissociation reactions $X_2 + M = 2X + M$, where X_2 is a diatomic molecule and M is a third body, were studied, over a wide temperature range, using two experimental techniques, flash photolysis and shock waves, and three methods of observation: absorption spectroscopy, emission spectroscopy and laser schlieren. Specifically, the recombination rate constants of iodine atoms, in the presence of various third bodies, were measured between 300 and 1200°K, and their temperature coefficients were determined. In the case of bromine atom recombination, it was possible to compare recombination and dissociation rate constants, obtained in the same laboratory, between 300 and 3000°K. A discrepancy, between low temperature flash photolysis data and high temperature shock wave data, which existed for some twenty years, was successfully resolved for a special and controversial case of bromine in argon.

In order to interpret the experimental results obtained, dissociation-recombination reactions were also studied using 3-D classical trajectory calculation techniques with Monte Carlo method of sampling. This technique allows a direct comparison between theory and experiments, because for dissociation-recombination reactions, the potential energy surfaces are known with a fair degree of accuracy from spectroscopic and molecular beam data. In particular, trajectory calculations for dissociation reactions were performed in some detail for I_2 and Br_2 , and non-equilibrium correction factors, which make a comparison between theoretical and experimental rate constants particularly meaningful, were calculated up to 6000°K. The agreement between the theory and experiment was found to be almost embarrassingly good; it will be necessary in the future to check in detail various assumptions used in theoretical calculations in order to make sure that the agreement is not spurious. Recombination of oxygen atoms was also studied using a trajectory method, and, again the agreement with experiment was found to be good. In order to check on some of the assumptions referred to above, the potential energy surface for $H + H + He$ collision was calculated ab initio. Use of such a surface would eliminate one of the important uncertainties in 3-D trajectory calculations. In order to study iodine dissociation, the emission from shock heated iodine was interpreted in detail spectroscopically. Using trajectory calculations, it was shown that, for iodine, the three body recombination in inert gas (Ar) is predominant below about 0.5 atmospheres. Above this pressure, four-and higher body collisions contribute to recombination. A model, which explains iodine recombination below 25 atmospheres and above about 100 atmospheres, was developed. This model yields in a good agreement with experiment.

In conclusion, an appreciable amount of experimental data on recombination-dissociation reactions was obtained, and a classical trajectory technique was developed to interpret data for these reactions.

AFOSR Program Manager: J. T. Viola, Lt Colonel

COMPLETED PROJECT SUMMARY

1. TITLE: Luminescent Transition Metal Complexes in Magnetic and Electric Fields.
2. PRINCIPAL INVESTIGATOR: Professor G. A. Crosby
Department of Chemistry
Washington State University
Pullman, Washington 99163
3. INCLUSIVE DATES: 15 September 1971 - 16 September 1975.
4. GRANT NUMBER: AFOSR-72-2207
5. COSTS AND FY SOURCE: \$79,603 FY72; \$97,642 FY73; \$64,973 FY74; \$55,984 FY75.
6. SENIOR RESEARCH PERSONNEL: Dr. R. J. Watts (9/71-2/72)
Dr. D. C. Baker
Dr. W. H. Elfring
7. JUNIOR RESEARCH PERSONNEL:

C. Araki	G. A. Merrell
T. Cremers	M. S. Pearce
J. L. Crosby	J. L. Sansregret
G. D. Hager	M. L. Stone
K. W. Hipps	K. A. Truesdell
D. E. Lacky	S. J. Westlake
8. PUBLICATIONS:

"Phosphorescence of Acetylacetonates of Trivalent Metals", G. A. Crosby, R. J. Watts and S. J. Westlake, Journal of Chem Phys, **55**, 4663 (1971).

"Quantum Efficiencies of Transition-Metal Complexes, III. The Effect of Ligand Substituents on Radiative and Radiationless Processes", R. J. Watts and G. A. Crosby, Journal of the American Chem Soc, **94**, 2606 (1972).

"A Comparison of $\pi\pi^*$ - $\pi\pi^*$ Interactions in Aromatics with $d\pi\pi^*$ - $\pi\pi^*$ Interactions in Iridium (III) Complexes", R. J. Watts and G. A. Crosby, Chemical Physics Letters **13**, 619 (1972).

"Excited States of Transition-Metal Complexes. A Spectroscopic Measurement of $d\pi\pi^*$ - $\pi\pi^*$ Interactions in Iridium (III) Complexes", R. J. Watts, G. S. Crosby and J. L. Sansregret, Inorganic Chemistry **11**, 1474 (1972).

"Absolute Quantum Efficiencies", a review, G. A. Crosby, J. N. Demas, and J. B. Callis, Journal of Research, National Bureau of Standards, **76A**, 561 (1972). and in the Proceedings of the Conference on Accuracy in Spectrophotometry and Luminescence Measurements, NBS, Gaithersburg, Maryland, March 22-24, 1972. NBS Special Publication 378, May 1973, p. 151.

"Radiative and Radiationless Decay Processes in Rhodium (III) Ammine Complexes", T. R. Thomas, R. J. Watts, and G. A. Crosby, Journal of Chemical Physics, **59**, 2123 (1973).

"Evidence for Multiple-State Emission from Ruthenium (II) Complexes", R. W. Harrigan, G. D. Hager, and G. A. Crosby, Chemical Physics Letters, **21**, 487 (1973).

- "Symmetry Assignments of the Lowest CT Excited States of Ruthenium (II) Complexes via a Proposed Electronic Coupling Model", R. W. Harrigan and G. A. Crosby, Journal of Chemical Physics, 59, 3468 (1973).
- "On the Appropriateness of Assigning Spin Labels to Excited States of Inorganic Complexes, G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., Journal of the American Chemical Society, 96, 629 (1974).
- "Molecular Sieves as Media for Growing Crystals", J. L. Sansregret and G. A. Crosby, Journal of Crystal Growth, 21, 313 (1974).
- "Geometrical Distortion and Spin-Orbit Splitting in Excited Transition-Metal Complexes", K. W. Hipps and G. A. Crosby, Inorganic Chemistry, 13, 1543 (1974).
- "Spectroscopic and Magnetic Evidence for Multiple-State Emission from Tris(2,2'-bipyridine)ruthenium(II) Sulfate", D. C. Baker and G. A. Crosby, Chemical Physics, 4, 428 (1974).
- "Investigation of the Temperature Dependence of Ruthenocene Photoluminescence", G. A. Crosby, G. D. Hager, K. W. Hipps, and M. L. Stone, Chemical Physics Letters, 28, 497 (1974).
- "Charge-Transfer Excited States of Ruthenium (II) Complexes. I. Quantum Yield and Decay Measurements", G. D. Hager and G. A. Crosby, Journal of the American Chemical Society, 97, 7031 (1975).
- "Charge-Transfer Excited States of Ruthenium(II) Complexes. II. Relationship of Level Parameters to Molecular Structure", G. D. Hager, R. J. Watts, G. A. Crosby, Journal of the American Society, 97, 7037 (1975).
- "Charge-Transfer Excited States of Ruthenium(II) Complexes, III. An Electron-Ion Coupling Model for $d\pi^*$ Configurations", K. W. Hipps, and G. A. Crosby, Journal of the American Chemical Society, 97, 7042 (1975).
- "Spectroscopic Investigations of Excited States of Transition-Metal Complexes", G. A. Crosby, Accounts of Chemical Research, 8, 231 (1975).
- "Luminescence as a Probe of Excited State Properties", G. A. Crosby, Proceedings of the Symposium on Inorganic Compounds with Unusual Properties, University of Georgia, Jan. 1975, Ed., R. B. King, in press.
- "Excited States of Mixed Ligand Chelates of Ruthenium(II) and Rhodium(III)", G. A. Crosby and W. H. Elfring, Jr., Journal of Physical Chemistry (proceedings of the Michael Kasha Symposium on Energy Transfer in Organic, Inorganic and Biological Systems, Florida State University, Jan, 1976), submitted.
- "Geometrical Distortion of the Excited States of d^6 Transition Metal Complexes: Systems of O_h and D_4h Symmetry", K. W. Hipps, G. A. Merrell, G. A. Crosby, Journal of Physical Chemistry (proceedings of the M. Kasha Symposium), submitted.
- "Luminescent Transition Metal Complexes in Magnetic and Electric Fields", G. A. Crosby, Final Tech Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

During the grant period several important developments pushed the laboratory closer to its long term goal of designing materials with predetermined electrooptical properties. New materials were synthesized that were highly luminescent and amenable to spectroscopic investigation. Magnetic switching of luminescence was demonstrated and the effect of external fields on excited states was quantified. Geometrical parameters of transition metal complex excited states were also determined.

The role of spin-orbit coupling in controlling excited state properties was elucidated both experimentally and theoretically, and a quantitative model of charge transfer excited states was enunciated that not only rationalized the known spectroscopic behavior of ruthenium(II) systems but is extensible to complexes of osmium(II) and iridium(III) as well.

New techniques were added that enhanced, manyfold, the power of the laboratory to probe excited states. These included the utilization of high power lasers, the extension of magnetic fields to ~80 kilogauss, the lowering of the accessible temperature range routinely to 21,5°K, and the employment of electronic means for decay time measurement. Magnetic circularly polarized luminescence was first observed from charge-transfer excited states and infrared optical double resonance was first successfully demonstrated for transition metal complexes.

AFOSR Program Manager: D. R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Energy Migration Involving Irradiated Solids.

2. PRINCIPAL INVESTIGATOR: Joseph Cunningham
University College Cork
Ireland

3. INCLUSIVE DATES: 1 April 1971 - 31 March 1976

4. GRANT NUMBER: AFOSR-71-2148

5. COST AND FY SOURCE: \$12,076 FY71; \$7,875 FY73.

6. RESEARCH PERSONNEL: N. Samman
B. Doyle
D. J. Morrissey
S. Corkery
H. Zainal
K. Hodnett
P. Meriaudeau
E. Finn
A. L. Penny

7. PUBLICATIONS:

"Flash Initiated Surface Reactions on ZnO and TiO₂ studies by Dynamic Mass Spectrometry", J. Cunningham and N. Samman, Chap 17 in Vol 4, Dynamic Mass Spectrometry, Price and Todd, pgs 247-271, 1976, Heyden and Sons, London.

"Photoeffects Involving Oxygen - 18 at Flash Illuminated ZnO and TiO₂ Surfaces", J. Cunningham, B. Doyle and N. Samman, JCS Farad. Trans. 1, 1976, Vol 72-1495-1498.

"Photoassisted Surface Reactions Studied by Dynamic Mass Spectrometry", J. Cunningham, E. Finn and N. Samman, Faraday Discussions of the Chem. Soc. No. 58, pgs 160-174.

"Reactions Involving Electron Transfer at Semiconducting Surfaces: VI, Electron Spin Resonance Studies on Dark and Illuminated Aqueous Suspensions of Zinc Oxides", J. Cunningham and S. Corkery, J. Phys. Chem., 1975, 79, 933-941.

"Reactions Involving Electron Transfer at Semiconductor Surfaces: V. Reactivity and Electron Paramagnetic Resonance of Electron Transfer sites on Rutile", J. Cunningham and A. L. Penny, J. Phys. Chem., 1974, 78, 870-875.

"New Technique for the Study of Selective Reactions at Rutile Surfaces", J. Cunningham, E. Finn and A. L. Penny, Chem. Sci., 1974, 6, 87-88.

"ESR Studies of Aqueous Suspensions of Zinc Oxides", J. Cunningham and S. Corkery, Chem. Phys. Ltr., 1973, 21, 421-425.

"Reactions Involving Electron Transfer at Semiconductor Surfaces: IV. Zinc Oxide Promoted Photoreductions in Aqueous Solutions at Neutral pH", J. Cunningham and H. Zainal, J. Phys. Chem., 1972, 76, 2362-2374.

"Reactions Involving Electron Transfer of Semiconductor Surfaces: III. Dissociation of Methyl Iodide over Zinc Oxide", J. Cunningham and A. L. Penny, J. Phys. Chem., 1972 76, 2353-2361.

"Energy Migration Involving Irradiated Solids", J. Cunningham, Final Tech Rpt.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

One particular aspect of 'Energy Migration in Irradiated Solids' has been emphasized in this research, namely the migration of energy from an irradiated solid to acceptor molecules of another phase in contact with the surface of the irradiated solid. Convincing evidence for this type of energy migration has been developed from studies at both "GAS/IRRADIATED SOLID" and "LIQUID/IRRADIATED SOLID" interfaces.

Initially, studies of such interfaces were made with closed systems under continuous illumination at low intensity. Using UV-photons of wavelengths absorbed by the solid substrate but not by the acceptor molecules in contact with the surface kinetics and mechanisms of photoassisted chemical changes were established for the system: Aqueous Electrolytes/ZnO; gaseous Methyl Halides/ZnO. An inherent limitation of the studies on closed systems with continuous low intensity illumination was their inability to distinguish between fast and slow photoassisted processes. Conclusions therefore rested upon detailed chemical study of long-term changes in acceptor molecules, brought about slowly by uv-illumination.

Later the technique of electron spin resonance was successfully applied, for the first time, to continuously circulating aqueous suspensions of zinc oxide in order to provide new insight into fast changes occurring simultaneously within the illuminated semiconducting solid. An important unifying feature of the detailed mechanisms developed for the energy transfer process at these illuminated interfaces was the central role played by electronic holes. Indications were obtained from these studies that quantum efficiencies of the observed chemical changes depended upon the extent to which electron-hole recombination processes competed with the chemical processes under study.

The research effort entered a new phase with the development at U.C.C. of unique apparatus for applying Dynamic Mass Spectrometry and related fast detection techniques to time resolve processes initiated at GAS/METAL OXIDE interfaces by 50 microsecond pulses of uv-photons. Initial studies of photoassisted interactions of flash illuminated ZnO or TiO₂ with ¹⁶O₂, N₂O or C₂H₅OH were expanded to include studies with isotopically enriched gases ¹⁸O₂, ¹⁴N¹⁵N¹⁶O and C₂D₅OD. The technique successfully time-resolved fast flash-initiated surface processes (such as surface photolysis, or photodesorption of chemisorbed oxygen, or release of alkene products from alcohol photodehydration) from slower surface processes, (such as post-flash uptake of oxygen by active surface sites, or release of products of alcohol photodehydrogenation). Implications of these results for 'Energy Migration within Solids and across their Interfaces' were presented at a Conference to be held under that title at University College Cork in September 1976.

AFOSR Program Manager: Lt Colonel J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Reactivity and Molecular Beams Scattering.
2. PRINCIPAL INVESTIGATOR: J. B. Fenn
Department of Engineering and Applied Science
Yale University
New Haven, Connecticut
3. INCLUSIVE DATE: 1 February 1972 - 31 March 1976.
4. GRANT NUMBER: AFOSR-72-2236.
5. COSTS AND FY SOURCE: \$62,867 FY72; \$31,869 FY74; \$30,188 FY75.
6. RESEARCH PERSONNEL: T. Nenner
H. Tien
P. J. Gale
7. PUBLICATIONS:
"Total Cross Section Measurements for the Scattering of Argon by Aliphatic Hydrocarbons", T. Nenner, H. Tien and J. B. Fenn, Journal of Chemical Physics 63, 5439 (1975).
"Long Range Attractive Forces for Hydrogen-Light Hydrocarbon Pairs", H. Tien, T. Nenner and J. B. Fenn, AlChE Journal 22, 405 (1976).
"Chemical Reactivity and Molecular Beam Scattering", J. B. Fenn, Final Technical Report.
8. ABSTRACT OF OBJECTIVE AND ACCOMPLISHMENT:

The present program has been concerned with measurements of integral cross sections for a wide variety of molecules in order to determine the so-called van der Waals or C_6 coefficients for the attractive portion of the pair wise potential. The C_6 designation stems from the fact that at the relatively large internuclear distances involved in total scattering cross sections for molecules without permanent dipole moments, the attractive force is due to induced-dipole induced dipole interactions which make the potential energy of the pair decrease as the sixth power of the internuclear distance. This C_6 is the coefficient of the $1/r^6$ term in most expressions for intermolecular potential, e.g., the familiar 12-6 or Lennard Jones potential. Originally, relative values of total cross sections over a variety of collision energies were planned to be obtained. Such measurements provide information about the depth and location of the so-called potential well. As the equipment and techniques developed, it was found that one could obtain absolute values of the total cross section with substantial accuracy and precision. Such absolute values at a particular and well defined velocity are perhaps the best way of obtaining C_6 values directly but there have been relatively few investigators who have been willing to take the pains necessary to achieve absolute values. Consequently, much of the effort was devoted to obtaining C_6 coefficients for a large number of molecular pairs. The desire to test a mixing rule which Kramer and Herschbach had found to be very effective in determining force constants between unlike molecules from their interaction behavior with a common partner was a stimulating factor. That is to say, if C_6 is known for the interaction of A with B and A with C, then the mixing rule will predict the C_6 for the interaction of B with C. Thus, if a set C_6 's is obtained for A with a family of molecules, an effective mixing rule would permit the prediction of C_6 for the interaction of any pair of molecules in the family. Clearly, an effective mixing rule together with a set of C_6 values for a particular molecule with a wide variety of collision

partners would comprise a very useful predictive tool in the estimation of transport and thermodynamic properties which depend upon the attractive forces between molecules. The essential steps in the experiments comprised: (1) generating a molecular beam by passing the core of a freely expanding supersonic jet through a conical collimating orifice commonly called a skimmer; (2) further collimating the beam and passing it through a scattering box; (3) measuring the intensity of the beam with an ionization gauge detector after it emerged from the scattering box. The results are summarized in tables and in addition to experimental values the tables include all values calculated from the Slater-Kirkwood approximation and from the mixing rule in light of experiments. The mixing rule does seem to work for the compounds which have been tested. In general, it gives values within less than five per cent of the terminal value. Therefore, the mixing rule can be used to calculate values of C_6 for practically any combination of molecules in the catalogue. Perhaps more surprising is the effectiveness of the Slater-Kirkwood approximation. It seems in general to give C_6 values which are rarely more than ten per cent in error and are usually much closer. Consequently, the results of Slater-Kirkwood calculations can be accepted for any molecules which are not in the catalog but which are reasonably similar in a chemical sense to those in the catalogue. It seems that an important consequence of this work is a substantial extension of the possibility of estimating thermodynamic and transport properties where attractive forces play a role and when there is a paucity of experimental data.

AFOSR Program Manager: J. T. Viola, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Ionization Processes Relevant to the Formation of New Materials

2. PRINCIPAL INVESTIGATOR: Professor Harlan L. Goering
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

3. INCLUSIVE DATES: 1 October 1970 - 31 August 1975

4. GRANT NUMBER: AFOSR-71-1972

5. COSTS AND FY SOURCE: \$50,000 FY71; \$22,000 FY74; \$22,000 FY75

6. SENIOR RESEARCH PERSONNEL: Dr. C. S. Chang
Dr. C. Chassin

7. JUNIOR RESEARCH PERSONNEL: H. W. Hasler
S. L. Trenbeath
M. L. Uhalde

8. PUBLICATIONS:

"Direct Determination of Enantiomeric Compositions with Optically Active Nuclear Magnetic Resonance Lanthanide Shift Reagents", H. L. Goering, J. H. Eikenberry, G. S. Koerner and C. J. Lattimer. J. Amer. Chem Soc., 96, 1493 (1974).

"Preparation and Determination of Absolute Rotations and Configurations of 6, 7-Dimethoxy-1, 2-dimethyl-exo-2-benzonorborenyl Derivatives", H. L. Goering, A. C. Backus, C. S. Chang and Divakar Masilamani, J. Org. Chem., 40, 1522 (1975).

"On the Regioselectivity of Lewis Acid Catalyzed Diels-Alder Reactions of Methylcyclopentadiene", H. L. Goering and C. S. Chang, J. Org. Chem., 40, 2565 (1975).

"Preparation and Determination of Absolute Configurations and Rotations of 1, 2-Dimethyl-5-norbornen-2-yl Derivatives", H. L. Goering and C. S. Chang, J. Org. Chem., 40, 3276 (1975).

"Ionization Processes Relevant to the Formation of New Materials", Harlan L. Goering, Final Tech Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research program involved investigation of the structure and chemistry of intermediates in ionic reactions (viz. carbonium ion reactions). The approach has been to determine symmetry properties of product forming intermediates and from these deduce structural details of these intermediates.

Kinetic, isotope tracer and stereochemical methods were used. In connection with the latter a new technique was developed which involves the use of optically active nmr shift reagents for the direct determination of enantiomeric compositions. The work in this area is described in one of the publications. With this technique, problems were solved that could not be handled by other methods.

Problems investigated in this project are summarized below.

Ion-pair return associated with solvolysis of α - and γ - phenylallyl p-nitrobenzoate has been investigated. With the α -isomer return results in re-formation of the original isomer. Return results in racemization and randomization of the carboxyl oxygen atoms. The rate of oxygen randomization exceeds that of racemization which shows return involves predominating (but not complete) retention of configuration. With the γ -isomer return results in isomeric rearrangement to the α -isomer. This does not result in complete randomization of the carboxyl oxygen atoms which shows that oxygen randomization does not detect all of the ion pair return in this system.

The 6,7-dimethoxy-exo-2-benzonorbornenyl system was also studied. The preparation of the required compounds and correlation of optical configurations necessary for this investigation have been published. Solvolysis of the optically active exo-p-nitrobenzoate leads to active products which shows that unlike with the parent secondary system, the intermediate is not a symmetrical bridged ion. Thus changing from secondary to tertiary changes ionization from assisted to unassisted.

Similar results were obtained with the 1,2-dimethyl-5-norbornen-2-yl-system. The preparation of the required compounds and correlation of optical configurations necessary for this study have been published. The synthesis required an investigation of the Lewis acid catalyzed Diels-Alder reaction of methylcyclopentadiene and this has also been published. Solvolysis of optically active exo-1,2-dimethyl-5-norbornen-2-yl-p-nitrobenzoate gives active products which shows that a symmetrical bridged cyclopropanecarbonyl cation is not involved. That a symmetrical bridged intermediate is involved in the parent 5-norbornen-2-yl system was confirmed by showing that solvolysis of optically active exo-p-toluenesulfonate gives racemic products.

In another study the solvolysis of exo-bicyclo (3.2.1) octan-6-yl-p-bromobenzenesulfonate was investigated. Here ion pair return results in racemization and randomization of the sulfoxyl oxygen atoms. The objectives of this work was to determine the symmetry properties of product forming intermediates and the amount and stereochemistry of ion pair return.

Ion-pair return associated with solvolysis of bicyclo (3.2.2)-nona-3,6,8-trien-2-yl p-nitrobenzoate was also investigated. In this system return results in isomeric rearrangement to the tricyclo (3.3.1.0^{2,8}) nona-3,6-dien-9-yl isomer. This rearrangement is intramolecular (no exchange with common ion salts) and results in complete randomization of the carbonyl oxygen atoms.

Also investigated was the stereochemistry of the conversion of allylic chlorides to cyclopropanes by hydroboration followed by 1,3-elimination. Pure E- and Z- β , γ -dimethylallyl chloride were converted to dimethylcyclopropane by this two-step process. The E chloride gives cis-dimethyl-cyclopropane and the Z chloride gives trans-dimethylcyclopropane. This establishes that the process is stereospecific and that the 1,3 elimination involves inversion of configuration of the carbon atom to which the boron is attached.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: The Absolute Measurement of Rate Constants for Some Key Reactions Involving Free Radicals
2. PRINCIPAL INVESTIGATOR: Dr. David M. Golden
Stanford Research Institute
Menlo Park, California 94025
3. INCLUSIVE DATES: 1 June 1971 - 31 December 1974
4. CONTRACT NUMBER: F44620-71-C-0103
5. COSTS AND FY SOURCE: \$47,700 FY71; \$49,633 FY72
30,400 FY73; 26,577 FY74; \$26,000 FY75
6. SENIOR RESEARCH PERSONNEL: Benson, Sidney W.
Golden, David M.
Postdoctoral Research Associates
Alfassi, Ze'ev B.
Beadle, Peter C.
Choo, Kwang Yul
Mendenhall, G. David
Perona, Michael P.
Piskiewicz, Leonard W.
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS:

"Very Low-Pressure Pyrolysis. VIII. The Decomposition of Di-t-Amyl Peroxide", M. J. Perona, D. M. Golden, Int. J. Chem. Kinetics, 5, 55 (1973).

"Very Low-Pressure Pyrolysis. IX. The Decomposition of Azoethane, Azoisopropane, and 2,2'-Azoisobutane", M. J. Perona, P. C. Beadle, and D. M. Golden, Int. J. Chem. Kinetics, 5, 495 (1973).

"An Absolute Measurement of the Rate Constant for Isopropyl Radical Combination", L. W. Piskiewicz, M. J. Perona, P. C. Beadle, and D. M. Golden, J. Amer. Chem. Soc., 96, 1645 (1974).

"Very Low-Pressure Pyrolysis (VLPP) of Alkanes: n-Butane, 2,3-Dimethylbutane, 2,2',3,3'-Tetramethylbutane, and Isobutane", Z. B. Alfassi, P. C. Beadle, and D. M. Golden, Int. J. Chem. Kinetics, 6, 359 (1974).

"Very Low-Pressure Pyrolysis (VLPP) of t-Butylmethyl Ether", K. Y. Choo, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinetics, 6, 631, (1974).

"The Pyrolysis of 2-Nitrosoisobutane and the Bond Dissociation Energies of Nitroso Compounds", K. Y. Choo, D. M. Golden, G. D. Mendenhall, and S. W. Benson, Int. J. Chem. Kinetics, 6, 813 (1974).

"Very Low-Pressure Pyrolysis of Nitroso- and Pentafluoro- Nitrosobenzene C-NO Bond Dissociation Energies", K. Y. Choo, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinetics, 7, 713 (1975).

"An Absolute Measurement of the Rate Constant for t-Butyl Radical Combination", K. Y. Choo, P. C. Beadle, D. M. Golden, and L. W. Piskiewicz, Int. J. Chem. Kinetics, 8, 45 (1976).

"An Absolute Measurement of the Rate Constant for Ethyl Radical Combination", D. M. Golden, K. Y. Choo, M. P. Perona, and L. W. Piskiewicz, Int. J. Chem. Kinetics, 8, 381 (1976).

9. ABSTRACT OF ACCOMPLISHMENTS AND OBJECTIVES:

The development of methods for measurement of absolute rate constants of radical processes important in combustion with specific attention to radical combination processes was the goal of this research.

A new method has been developed for the determination of absolute rate constants for the recombination of free radicals. The method is an extension of the VLPP technique and was applied to the study of the recombination of ethyl radicals, isopropyl radicals, and t-butyl radicals. Application of the method required a preliminary study of the decomposition of certain radical sources under VLPP conditions. The radical sources studied are: di-t-amyl peroxide, azoethane, azoisopropane, 2,2'-azoisobutane, and nitrosoisobutane. In the case of the azo compounds, the flow dependence of k_{uni} was used to estimate collisional efficiencies. It was found that alkyl radicals are removed by a first-order wall process. The rate constant for this process was found to be dependent on the nature of the wall.

The rate constant for ethyl radical combination was determined at 845 and 878°K using the very low-pressure pyrolysis (VLPP) technique. The value at both temperature is $\log (k_r/M^{-1} \text{ sec}^{-1}) = 9.7 \pm 0.3$. Transition state models combined with RRKM calculations indicate that $k_r/k_r^{oo} \sim 1/2$ under these conditions, so that $\log (k_r^{oo}/M^{-1} \text{ sec}^{-1}) \sim 10 \pm 0.3$.

Absolute values of the rate constant for isopropyl radical combination have been determined over the temperature range 683-808°K. The value $\log (k_r/M^{-1} \text{ sec}^{-1}) = 9.5 \pm 0.2$ fits all the data, leading to the conclusion that the temperature dependence, if any, is slight. It has been found that isopropyl radicals react heterogeneously in a first-order manner with fused silica, probably to produce propylene.

The rate constant for t-butyl radical combination was determined over the temperature range 620-690°K, using the very low-pressure pyrolysis (VLPP) technique. The value of the combination rate constant, $\log k_r/M^{-1} \text{ sec}^{-1} = 8.7 \pm 0.3$ and the disproportionation combination ratio, $k_d/k_r \approx 3$, were independent of temperature in the small range studied here.

The four species (n-butane, 2,3-dimethylbutane, 2,2',3,3'-tetramethylbutane, and isobutane) were decomposed under VLPP conditions at temperatures in the vicinity of 1100°K. Three model transition states were constructed that fit the low-pressure data thus obtained and that also yield: (1) $E_{298} = \Delta E_{298}$; (2) E_{1100} ; (3) $\log A_{1100} = 16.4/\text{C-C bond broken}$. The prediction of these models as to values of the high-pressure rate constants for bond scission and the reverse rate constants (radical combination) are compared with existing data.

Study of the pyrolysis, $t\text{Bu-NO} \xrightarrow{1} t\text{Bu} + \text{NO}$ by VLPP yields for the Arrhenius parameters $k_1 = 10^{16.0 \pm 0.5 - (38 \pm 1)/\theta} \text{ sec}^{-1}$, where $\theta = 2.303 RT$ in kcal/mole. This yields for the high pressure, second-order recombination of $t\text{Bu} + \text{NO}$, $k_{-1} = 2.0 \times 10^9 \text{ l/mole-sec}$. For a competing reaction to -1, $t\text{Bu} + \text{NO} \xrightarrow{4} i\text{-C}_4\text{H}_8 + \text{HNO}$, $k_4(600^\circ\text{K}) < 10^{7.5} \text{ l/mole-sec}$, so that $E_4 > 4.2 \text{ kcal/mole}$. The bond dissociation energy $\Delta H^\circ(t\text{BuNO}) = 40 \pm 1 \text{ kcal/mole}$. A new free-volume model for the transition state for dissociation is shown to fit the data.

The high pressure absolute rate constants for the decomposition of nitrosobenzene and pentafluoro-nitrosobenzene were determined using a very low-pressure pyrolysis (VLPP) technique. $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{NO})$, $\Delta H_f^\circ(\text{C}_6\text{F}_5\text{NO})$, and $\Delta H_f^\circ(\text{C}_6\text{F}_5\cdot)$ could be estimated from our kinetic data and group additivity. The values are 48.1 ± 1 are -130.9 ± 2 kcal/mole, respectively.

The thermal decomposition of t-butylmethyl ether has been studied using the VLPP technique. The recommended Arrhenius parameters for the molecular elimination reaction (1) are $A(800^\circ\text{K}) = 10^{13.9} \text{ sec}^{-1}$ and $E_a(800^\circ\text{K}) = 59.0 \pm 1.0$ kcal/mole.

AFOSR Program Manager: John T. Viola, Lt Colonel

COMPLETED PROJECT SUMMARY

1. TITLE: Effect of Structure on Physical Properties of Polymers.

2. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002

3. GRANT NUMBER: AFOSR-72-2170

4. INCLUSIVE DATES: 1 November 1971 - 28 February 1976.

5. COSTS AND FY SOURCE: \$61,009 FY72; \$30,040 FY74; \$30,030 FY75.

6. SENIOR RESEARCH PERSONNEL: Dr. H. Goettler
Dr. R. Hammel
Dr. O. Heybey
Dr. W. Wenig

7. JUNIOR RESEARCH PERSONNEL: P. Alexandrovich
G. R. Dever
J. R. Fried
L. Kleiner
R. Neira
K. Rozkuszka
E. B. Wilusz
S. Wunder

8. PUBLICATIONS:

"Poly(alkyl α -chloroacrylates): Preparation and Properties of Methyl, Ethyl and Isopropyl Polymers of Varied Tacticity", G. R. Dever, F. E. Karasz, W. J. MacKnight and R. W. Lenz, J. Poly. Sci., Poly. Chem. Edn., 13, 2151-2179 (1975); G. R. Dever, Ph.D. Thesis, University of Massachusetts, 1974.

"Poly(alkyl α -chloroacrylates): Tacticity Analysis from 300 MHz NMR Spectra", G. R. Dever, F. E. Karasz, W. J. MacKnight and R. W. Lenz, J. Poly. Sci., Poly. Chem. Edn., 13, 1803-1818 (1975).

"Poly(alkyl α -chloroacrylates): Transitions and Relaxations", G. R. Dever, F. E. Karasz, W. J. MacKnight and R. W. Lenz, Macromolecules, 8, 439-443 (1975).

"Water Vapor Transport in Hydrophilic Urethanes in Permeability of Plastic Films and Coatings", H. B. Hopfenberg, Ed., Plenum Press, 1975 by J. L. Illinger, N. S. Schneider and F. E. Karasz, pp. 183-197.

"Self-Beat Spectroscopy and Molecular Weight", N. C. Ford, F. E. Karasz, R. Gabler, Advances in Chemistry Series, 125, 25-54 (1973).

"Quasi-Elastic Light Scattering Studies of an Ethyl Acrylate-Acrylic Acid Copolymer", S. Wunder, F. E. Karasz, N.C. Ford, Bull. Am. Phys. Soc., 21, 348 (1976) abstract.

"Experimental Study of Flexural Vibrations in Thick Beams", O. Heybey and F. E. Karasz, J. Appl. Phys., 47, 3252-3260 (1976).

"Acoustical Frequency Dynamical Mechanical Studies", O. Heybey and F. E. Karasz, Bull. Am. Phys. Soc., 18, 461 (1973) and in press.

"R. Neira-Lemos, Ph.D. Thesis", University of Massachusetts, 1975 to be published.

- "Structure and Properties of the System: Poly(2,6-Dimethyl Phenylene Oxide)--Isotactic Polystyrene, Small Angle X-Ray Studies", W. Wenig, F. E. Karasz and W. J. MacKnight, J. Appl. Phys., **46**, 4194-4198 (1975).
- "Structure and Properties of the System: PP0-i-PS. Wide Angle X-Ray Studies", R. Hammel, F. E. Karasz and W. J. MacKnight, J. Appl. Phys., **46**, 4199-4204 (1975).
- "Morphological Studies of Semicrystalline PP0", F. E. Karasz, W. Wenig, R. Hammel and W. J. MacKnight, Macromolecules **9**, 253-257 (1976).
- "Dielectric Properties of the PP0-copoly(PS-PCS) System", F. E. Karasz, W. J. MacKnight, J. J. Tkacik, Polymer Preprints, **15**, 415-420 (1974).
- "Compatibility of PP0 with Copolymers of Styrene and p-Chlorostyrene", J. R. Fried, F. E. Karasz and W. J. MacKnight, Bull. Am. Phys. Soc., **21**, 237 (1976).
- "Thermally Stimulated Discharge in Polymer Electrets", P. Alexandrovich, F. E. Karasz and W. J. MacKnight, J. Appl. Phys., in press (Nov., 1976).
- "Pressure Effects on Thermochemical Properties of Polyethylene", K. Rozkuszka and F. E. Karasz, Bull. Am. Phys. Soc., **21**, 267 (1976). Abstract to be published.
- "Low-Frequency Damping in Polymethyl Methacrylate as a Function of Temperature and Pressure", H. J. Goettler, F. E. Karasz and C. W. Nelson, Bull. Am. Phys. Soc., **20**, 312 (1975) in press.
- "Transitions in Poly(diethyl Siloxane)" C. L. Beatty and F. E. Karasz, J. Poly. Sci., Poly. Phys. Edn. **13**, 971-975 (1975).
- "Dielectric Properties of Poly(diethyl Siloxane)", J. Pachan, F. E. Karasz and C. L. Beatty, J. Poly. Sci., Poly. Phys. Edn., **13**, 976-982 (1975).
- "Dielectric Properties of Poly-ε-caprolactone", E. B. Wilusz and F. E. Karasz, Polymer Preprints, **16**, 584-588 (1975).
- "Brominated Polypentenamer and Nitrile Derivatives", J. R. Fried, F. E. Karasz and W. J. MacKnight, J. Appl. Poly. Sci., **19**, 3381-3383 (1975).
- "On the Separation of Fusion Entropy into Configurational and Volume Expansion Terms", F. E. Karasz and P. Couchman, Macromolecules, **9**, in press (Dec. 1976).
- "Temperature Variation in the Surface Energy of Crystalline Solids" P. R. Couchman and F. E. Karasz, Int. J. of Phys. and Chem. Solids, in press.
- "On the Relation Between Surface Energy, Melting Temperature and Interatomic Separation", C. L. Reynolds, F. E. Karasz and P. R. Couchman, Phil. Mag., in press.
- "Dielectric Properties of Polymers", F. E. Karasz, Ed., Plenum Press, N.Y. 1972.
- "Transitions in Polymer Blends", F. E. Karasz and W. J. MacKnight, Chapter V, in Polymer Compatibility, D. R. Paul, Ed., in press.
- "Reports on Progress in Polymer Physics in Japan, Vol. XVIII", F. E. Karasz, J. Poly. Sci., Part B, **14**, 432 (1976).
- "Advances in Polymer Science, Vol. 13: Thermal Analysis", F. E. Karasz, Analytical Chem., **47**, 353A (1975).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Air Force requirements in the area of polymers for adhesives, sealants, surface coverings, wire insulators and structural materials have become increasingly demanding in the physical properties required.

The overall objectives of the program has been to examine the effect of variations in the chemical and stereochemical structure of a polymer on its physical, mechanical and electrical properties. Such information is of interest both on a fundamental level and because of its implications in the design of macromolecular structures for specific applications. Within this general direction a number of different investigations were undertaken.

The effect of configuration--stereochemical structure--in poly- α -chloroacrylic acid esters was studied. These unsymmetrically disubstituted vinyl polymers showed a large dependence of T_g on tacticity in accordance with theory developed earlier. Other transitional and thermodynamic properties were also found to be structure-dependent. The effect of chemical structure was demonstrated in a different context in an investigation of the interaction of small molecules, especially water, with a series of segmented polyurethanes with systematically varying soft segment compositions. Decreasing hydrophilicity of the latter substantially affected transport properties. Evidence for the amorphous nature of the bound water layer was obtained from comparison of the glass transition behavior of the dry and water-containing polymers.

The effect of structure is particularly profound in the area of polymer-polymer compatibility. Extremely small changes in composition in either or both constituents of a given binary system may be sufficient to remove the system from a compatible to an incompatible regime. These and other effects were studied in considerable detail in an on-going investigation of interactions between poly(2,6-dimethyl phenylene oxide) and polystyrene, together with stereochemical and chemical modifications of the latter polymer. Thermodynamic, mechanical and electrical properties of these systems were studied with the goal of determining characteristics general to all compatible systems and of finding methods of predicting behavior.

The solid and liquid state properties of a given ensemble of polymers are functions of temperature, pressure, and in the case of visco-elastic related phenomena, stress frequency. We have studied the effect of these three parameters in a dynamical mechanical investigation of polymethyl methacrylate. Although important, the effect of pressure on mechanical relaxation of any polymer has only rarely been examined. In the study undertaken here the effect of pressure on both the α - and β -relaxations was analyzed. In another experiment, apparatus for measuring the effect of pressure on the lattice dimensions of polymer crystals was developed and tested in a broad study of the polyethylene lattice. The linear compressibilities thus obtained permitted a detailed comparison with theoretically predicted equations of state for this macromolecule. A further dynamical mechanical experiment was concerned with resonant vibrations in thick beams. From measurements and analysis of higher mode resonances the contributions of shear and elongational deformation could be separately obtained, thereby providing a complete elastic characterization of an isotropic material. We have also been concerned in one study with the properties of solvated macromolecules, in this case an ionizable copolymer of acrylic acid and ethyl acrylate. The experimental technique used was quasi-elastic light scattering in which the spectral broadening and shape of light scattered from spontaneously occurring density fluctuations within the solution is measured with a homodyne spectrometer. The

translational diffusion constant is obtained from such data together with the effects of hydrodynamic and thermodynamic solute-solute and solute-solvent interactions as a function of solute concentration, pH, ionic strength and temperature. A number of miscellaneous studies dealing with bulk properties of polymers were completed.

AFOSR Program Manager: Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Infrared Spectra of Fluid Films under Conditions of Incipient Bearing Failure, Phase I.

2. PRINCIPAL INVESTIGATOR: Dr. James L. Lauer
Sun Oil Company
Applied Research & Development Department
P.O.Box 1135
Marcus Hook, PA 19061

3. INCLUSIVE DATES: 1 January 1974 - 30 June 1976

4. CONTRACT NUMBER: AFOSR-F44620-74-C-0038

5. COSTS AND FY SOURCE: \$20,000 (government) + \$ 9,213 (Sun Oil Co.) FY 73;
\$40,000 (government) + \$26,667 (Sun Oil Co.) FY 74;
\$44,992 (government) + \$29,995 (Sun Oil Co.) FY 75

6. SENIOR RESEARCH PERSONNEL: Dr. James L. Lauer
Mr. Melvin E. Peterkin

7. JUNIOR RESEARCH PERSONNEL: None.

8. PUBLICATIONS:

"Infrared Emission Spectra of Liquids in a Diamond Anvil Cell by Interferometry", James L. Lauer and M. E. Peterkin, Applied Spectroscopy 29, 78 (1975).

"Infrared Emission Spectra of Liquids in a High Pressure Diamond Cell with the Beckman-RIIC FS-720 Interferometer", James L. Lauer and M. E. Peterkin, The Transform, No. 3, p. 22-25, (September 1974) (R.J. Jakobsen, Editor, Battelle Memorial Institute).

"Analysis of Infrared Spectra of Fluid Films in Simulated EHD Contacts", James L. Lauer and M. E. Peterkin, Lubrication Technology, Vol 97, Series F, No. 2, p. 145-50 (April 1975).

"Study to Define Behavior of Liquid Lubricants in an Elastohydrodynamic Contact", James L. Lauer, NASA CR-134671, October 17, 1974. Prepared for National Aeronautics and Space Administration, NASA Lewis Research Center, Cleveland, Ohio.

"Infrared Emission Spectro of Liquids in a Diamond Anvil Cell by Interferometry", J. L. Lauer and M. E. Peterkin, Applied Spectroscopy, 29, 78 (Jan 75).

"Infrared Emission Spectra of Elastohydrodynamic Contracts", J. L. Lauer and M. E. Peterkin, J. Lubrication Technology, 98, 230-235 (1976).

"Infrared Emission Spectra of Fluid Films", J. A. Lauer and M. E. Peterkin, American Laboratory, Vol 7, No. 11, pp. 27-33 (November 1975).

"Analysis of Infrared Spectra of Elastohydrodynamic Lubricant Films", J. A. Lauer and M. E. Peterkin, Petroleum Division Preprints, American Chemical Society National Centennial Meeting, Symposium on Lubricant Properties in Thin Lubricating Films, New York City, April 6, 1976, pp.48-56.

"High Pressure Interferometry", J. L. Lauer in "Fourier Transform IR: Applications to Chemical Systems", J. R. Ferraro and L. J. Basile, editors, to be published in the spring of 1977 by Academic Press, New York, 75 pp., figures and tables.

"Infrared Emission Spectra from Operating Elastohydrodynamic Sliding Contacts", J. L. Lauer, NASA CR-134973, March 8, 1976. Prepared for National Aeronautics and Space Administration, NASA Lewis Research Center, Cleveland, Ohio.

"Traction and Lubricant Film Temperature as Related to the Glass Transition and Freezing", J. L. Lauer and M. E. Peterkin, to be published in Can. J. of Spectroscopy 21, Sept/Oct 1976.

"Traction and Lubricant Film Temperature as Related to the Glass Transition and Freezing", J. L. Lauer and M. E. Peterkin, Lubrication, to be published in 1977.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Under conditions of high stress moving parts of machinery, such as bearings or gears, are prevented from self-destruction by the interposition of extremely thin films of lubricants. Since failure is unlikely to occur without warning, examination of the lubricant in operating bearings approaching failure appeared to be a procedure promising to provide clues on reasons for failure and thus to provide a basis for improved lubrication. The method of analysis chosen was infrared emission Fourier spectrophotometry, a relatively new procedure which is particularly well adapted to thin film analysis and which -- in contrast to absorption spectrophotometry -- requires only one window transparent to infrared radiation. The fluid film heated by internal friction during bearing operation takes the place of the source for the spectrophotometer.

This phase of the work was (1) to demonstrate that infrared emission spectrophotometry can be applied to bearing contact situations, (2) to provide background in the form of calibration spectra applicable to such situations, and (3) to show the potential of the method in specific instances relevant to the failure problem. Very substantial obstacles had to be overcome: (1) very weak radiant power passed through the window and most of it originating from the solid boundary surfaces rather than from the lubricant film; (2) different fluid and solid surface temperatures; (3) ignorance regarding expected lubricant spectral changes with pressure, temperature, shear rate, and fluid/glass transition. Accordingly most of the effort involved the development of appropriate hardware and background information.

Bearing failure is most likely to occur when the solid surfaces bounding the lubricant are elastically deformed under so-called elastohydrodynamic (EHD) lubrication. Curved surfaces are then flattened over the "Hertzian" contact region. Furthermore, sliding is more severe than rolling, hence a loaded bearing ball rotating, i.e., sliding, on a plate was adapted as a model to represent a bearing bearing failure. By making the plate a diamond window, some heat generated in the contact can be transmitted as radiation for spectroscopic analysis. Since diamond is transparent throughout most of the infrared spectrum, the examination of spectral changes even in the "fingerprint" infrared region (10-15 μm) and in the lattice region ($>15\mu\text{m}$) is feasible. For calibration of the spectral information of the ball-on-plate apparatus a high-pressure diamond anvil cell was used as a "simulated contact". Its sample volume could be subjected to most of the conditions likely to prevail in a sliding EHD Hertzian contact (thickness $<2\mu\text{m}$, open area $\sim 0.25\text{mm}^2$, pressures

0-75 kbar, temperatures 0-200°C) except for shear. As typical fluids, an ester, polyphenyl ether (5P4E), a standard petroleum lubricant, and a so-called "traction" fluid were used. A Fourier infrared interferometer was adapted for all the spectroscopic work.

In the initial stages of the program, absorption spectra were obtained with the diamond cell under various temperatures and pressures. From the splitting of the $725\text{-}735\text{ cm}^{-1}$ CH rocking frequency band it was possible to infer crystallization at certain pressures and temperatures for the ester and the petroleum fluid. Entrance optics were built to convert the Fourier infrared interferometer into an emission micro-interferometer and it was possible to show the equivalence between absorption and emission spectra at the same temperature and pressure. This achievement constitutes a major breakthrough; for while infrared emission spectra of thin layers of organic material on metal substrates have been obtained by previous investigators, spectra from radiating areas as small as Hertzian contacts and at average temperatures as low as 30-50°C very nearly represent the limit of today's instrumental capability.

A model ball-on-plate apparatus was then built for the same interferometer and entrance optics. The window was located at the bottom of a cup containing the test fluid. A loaded bearing ball rotated about a horizontal axis while sliding over the window provided the bearing contact. The apparatus was located above the interferometer entrance optics. Precise alignment of the contact region on the optic axis and in the focal plane of the entrance optics was essential and was achieved. Indeed it was possible to obtain "dynamic" infrared spectra from the fluids under various conditions prevailing in the Hertzian area.

The analysis of the spectra gave some surprising results. It was possible to deduce both ball surface and fluid film temperatures from the spectra. When temperature differences were plotted against shear rate, the data for all the fluids fell on practically the same curve, which showed a peak corresponding to an intermediate shear rate. The traction fluid reached the highest temperature difference under equal conditions. However, the polyphenyl ether would reach the highest absolute temperature at high shear rates -- just prior to bearing failure. At the same time its spectrum would change, indicating decomposition. Another observation was an intensity change with shear rate of one band, which could be related to polarization of the emitted radiation. The mechanism for it might well be streaming birefringence, although other explanations have not yet been excluded.

A separate but related achievement was the design and construction of apparatus to determine pressure and state of material in the diamond anvil cell from the peak frequency and width of the fluorescence band of ruby crystals contained within the sample. In contrast to earlier opinion considering traction as caused by glassy particles in the contact zone, the traction fluid tested needed higher pressures to be converted into the glassy state than the other fluids and must therefore function by a different mechanism.

Work was started toward a reliable determination of the state of the fluid (liquid or glassy) from the dynamic infrared spectra.

AFOSR Program Manager, Lt Col R.W.Haffner

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COMPLETED PROJECT SUMMARY

1. TITLE: AFOSR Program at UCLA in the Chemistry of Materials Under Extreme Environmental Conditions.

2. PRINCIPAL INVESTIGATOR: Dr. Willard F. Libby
Department of Chemistry
UCLA
Los Angeles, California

3. INCLUSIVE DATES: 1 December 1970 - 31 March 1975

4. GRANT NUMBER: AFOSR-71-2019

5. COSTS AND FY SOURCE: \$93,970 FY71; \$94,192 FY72; \$63,000 FY73; \$75,000 FY74; \$25,000 FY75

6. SENIOR RESEARCH PERSONNEL:

Dr. Rainer Berger	Dr. Howard Katzman
Dr. Paul Corneil	Dr. Leona Libby
Dr. E. E. Ferguson	Dr. Paul C. Maybury
Dr. N. Fukuta	Dr. Joseph Speckbach
Dr. Abdolah Hendifar	Dr. George Zimmerman

7. JUNIOR RESEARCH PERSONNEL:

Saulius Alkaitis	John Marshall
Dale Barry	J. Moss
Mitchell Cooper	Randy Murphy
Edward Greer	Louis Pandolfi
Sim Hoffman	Pat Payton
John Kerridge	Lee Pedersen
Joel Leventhal	Mike Sheridan
Jeff London	Saburo Yashita

8. PUBLICATIONS:

"Promising Catalyst for Auto Exhaust", W. F. Libby, Science 171, 499 (1971).

"Mechanism for the Fixation of Nitrogen by Lightning", E. E. Ferguson and W. F. Libby, Nature, 229, 37 (1971).

"Polymer Production in the Radiolysis of Methane, Ethane, and Ethylene Solutions in Liquid Argon", M. E. Sheridan, E. Greer and W. F. Libby, J. Amer. Chem. Soc., 94, 2614 (1972).

"Sintered Diamond Compacts with a Cobalt Binder", H. Katzman and W. F. Libby, Science, 192, 1132 (1972).

"One-Parameter Equation of State for Metals and Certain Other Solids", L. M. Libby and W. F. Libby, Proc. Nat. Acad. Sci., 69, 3305 (1972).

"Unseparated Rare Earth Cobalt Oxides as Auto Exhaust Catalysts", Lee A. Pedersen and W. F. Libby, Science 176, 1355 (1972).

"Possible Formation of Singlet Oxygen in the Radiolysis of Water Under High Pressure Oxygen", S. A. Alkaitis and W. F. Libby, Nature Physical Science, 244, 143 (1973).

"Catalyzed and Uncatalyzed Dissolution of Anhydrous Chromic Chloride in Aqueous Solution", A. Hendifar, W. F. Libby and George Zimmerman, J. Phys. Chem, 78, 1993 (1974).

"Non-Etching Optical Detection of Fission Tracks Using Teflon", P. C. Maybury and W. F. Libby, Nature, 254, 209 (1975).

"AFOSR Program at UCLA in the Chemistry of Materials Under Extreme Environmental Conditions", W. F. Libby, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research included work on rare earth perovskites as catalysts, radiation chemistry, radiation damage in crystals, and electron tunneling in chemistry.

Research on rare earth perovskites indicates that these substances show promise as replacements for platinum catalysts. The catalytic properties of the transition element compounds appear to be due to the d orbitals which can form several bonds simultaneously on a single atom, bonds which are not too strong to be broken and yet are strong enough to dissociate ordinary Sp bonds.

In the radiation chemistry area research was concentrated on setting a body of principles generally applicable using data obtained on hydrocarbons in condensed systems at low temperature. In work on the polymer production from the gamma radiolysis of methane and other light hydrocarbons dissolved in liquid argon, it was found that the gamma rays ionize the argon solvent since it is heavier and more abundant but that the effect on the solvent methane is as though it were preferentially attached. This is interpreted as being due to electron transfer by a tunnelling process from the solute methane, ethane, or ethylene to the ionized argon, resulting in the formation of the hydrocarbon ion which then proceeds to react. A series of polymers of methane is produced beginning with ethane and culminating in a $C_{20}H_{40}$ polymer.

It was found that very high pressures have effects on organic materials which are different from temperature effects. Reactions can be made to occur at liquid nitrogen temperatures at 60,000 atmospheres which do not occur, or only to a small extent, at room temperature and the same pressures.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Structure and Properties of Glasses
2. PRINCIPAL INVESTIGATORS: Dr. P. B. Macedo and
Dr. T. A. Litovitz
Vitreous State Laboratory
Catholic University of America
Washington, D.C., 20064
3. INCLUSIVE DATES: 1 September 1971 - 31 August 1976
4. GRANT NUMBER: AFOSR-72-2203
5. COSTS AND FY SOURCE: \$82,050, FY72; \$82,000 FY73; \$82,032, FY74; \$82,000 FY75;
\$85,000 FY76
6. SENIOR RESEARCH PERSONNEL: Dr. C. T. Moynihan
Dr. P. K. Gupta
Dr. J. H. Simmons
7. JUNIOR RESEARCH PERSONNEL: A. J. Easteal
J. A. Wilder
J. Tucker
M. A. DeBolt
N. Saad
B. E. Dom
Fizika i Khimiya Stekla
C. C. Lai
C. J. Montrose
J. F. Dill
P. Drake
P. B. Elterman
R. P. Mocller
H. Sasable
R. Scully
L. P. Boesch
N. L. Laborge
F. S. Howell
R. A. Bose
T. J. Higgins
V. Volterra
D. C. Tran
E. P. Donovan
G. P. Srinivasan
R. Colella
A. Sarkar
R. Mahoney
A. Napolitano
8. PUBLICATIONS:

"Analysis of Composition Fluctuation Lifetimes in a Critical Oxide Mixture by
Volume Relaxation Spectroscopy", J. H. Simmons and P. B. Macedo, J. Non-Cryst. Sol.
11, 357-367 (1973).

"On the Determination of Spinodal Temperature by Electron Microscopy", A. Sarkar,
P. K. Gupta, G. R. Srinivasan, V. Volterra and P. B. Macedo, J. Chem. Phys. 59,
4246-4249 (1973).

"Small Angle X-Ray Scattering Study of Spinodal Decomposition in the B_2O_3 - PbO - Al_2O_3 System", G. R. Srinivasan, R. Colella, V. Volterra, Phys. Chem. Glasses, **14**, 90-95 (1973).

"Theoretical Analysis of Miscibility Gaps in the Alkali-Borates", P. B. Macedo and J. H. Simmons, J. Res. Nat. Bur. Stds., **78A**, 53.

"Effect of Subcritical Microstructure on the Viscosity of a Sodium Borosilicate Glass", R. Mahoney, G. R. Srinivasan, P. B. Macedo, A. Napolitano and J. H. Simmons, Phys. Chem. Glasses **15**, 24 (1974).

"Electron Microscope Observations of Phase Separation near Spinodal Boundary in a Sodium Borosilicate Glass", G. R. Srinivasan, A. Sarkar, P. K. Gupta and P. B. Macedo, J. Non-Cryst. Sol. **20**, 141-148 (1976).

"Ultrasonic Relaxation Studies in Potassium-Borate Melts", R. Scully, J. H. Simmons, and P. B. Macedo, J. Non-Cryst. Sol. **12**, 18-34 (1973).

"Viscoelastic Relaxation in B_2O_3 ", C. C. Lai, P. B. Macedo and C. J. Montrose, Tenth Int'l Cong. on Glass **11**, 68-72 (1974).

"Dependence of the Glass Transition Temperature on Heating and Cooling Rate" C. T. Moynihan, A. J. Easteal, J. A. Wilder, and J. Tucker, J. Phys. Chem. **78**, 2673 (1974).

"Electrical and Mechanical Relaxations in a Mixed-Alkali Silicate Glass", T. J. Higgins, L. P. Boesch, V. Volterra, C. T. Moynihan, and P. B. Macedo, J. Am. Ceram. Soc. **56**, 334 (1973).

"Decay Function for the Electric Field Relaxation in Vitreous Ionic Conductors", C. T. Moynihan, L. P. Boesch and N. L. Laberge, Phys. Chem. Glasses, **14**, 122 (1973).

"Electrical Relaxation in a Glass-Forming Molten Salt", F. S. Howell, R. A. Bose, P. B. Macedo and C. T. Moynihan, J. Phys. Chem. **78**, 639.

"Heat Capacity and Structural Relaxation of Mixed-Alkali Glasses", C. T. Moynihan, A. J. Easteal, D. C. Tran, J. A. Wilder, and E. P. Donovan, J. Am. Ceram. Soc., **59**, 137 (1976).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Air Force interest in glass as a basic constructive material is two fold. As a fiber optic material its unique properties make it useful for special communicative applications where resistance to damaging radiation is desired. Also special glasses are desired for high strength, impact resistant enclosure for aircraft.

Research has been performed on glasses and glass-forming liquids which was directed toward (1) microstructure and phase separation, (2) viscoelastic and structural relaxation in molten glasses and (3) electrical relaxation phenomena.

Interest from scientific and technological areas has long been evident in the analytical description of miscibility gaps in oxide glasses. These analytical expressions have been sought to serve both as a basis for physical modeling of phase separation thermodynamics and as a simple means for predicting phase separation temperatures for oxide mixtures with compositions of interest. A thermodynamic approach based on regular mixing concepts was applied to modeling phase separation in alkali-borate glasses. It was found to be quite successful in describing the miscibility gap boundaries (or coexistence curve). The concept

which must be introduced to accomplish this was the assumption that the glass-former phase is structurally represented by a complex molecule and the glass-former-modifier phase by a stoichiometric compound. This transformation symmetrizes the coexistence curve.

The regular mixing equation appears to represent the data well when an additional entropy of mixing arising from changes in the internal degrees of freedom of the system is included in the calculation. Following this approach, five systems were treated successfully. The complex boron trioxide molecule $[(B_2O_3)_5]$ was used in the regular mixing analysis of all the borate systems considered, since the miscibility gaps occurred approximately within the same temperature range.

The implications of such an approach are interesting but not surprising. The existence of complex glass-former structures in the melt appears to offer a good explanation for the behavior of an increasing number of physical properties of molten oxide glasses. An actual geometrical description of the complex boron trioxide structure was not possible by this analysis since thermodynamic treatments do not afford structural descriptions.

Composition fluctuations present in the supercritical region (the single phase region near the critical point of an immiscibility dome) of a multicomponent-glass can be observed by replica electron microscopy provided (1) it is possible to quench these (composition) fluctuations to room temperature through a large two phase region and (2) an etching agent is available which is sufficiently sensitive to expose small compositional variations. The isothermal growth of such fluctuations in the supercritical region of a sodium borosilicate glass having a small amount of alumina was studied. The main effect of alumina is to lower the immiscibility dome and thereby bring the supercritical region in a high viscosity domain.

Of particular interest in these studies is the temperature dependence of the equilibrium fluctuation size, $\lambda(T, C_0)$. [$\lambda(T, C_0)$ is the mean intercept length of a micrograph of a sample of average composition, C_0 , which has been heat treated at a temperature, T , for long time.] These results are closely approximated by a power law $\lambda(T, C_0) = K[T - T_0(C_0)]^{-\nu}$ (1) with three independent parameters: K , ν and T_0 . For the two glasses studied:

(i) the exponent, ν , seems to be the same for both glasses and is about 0.5 ± 0.005 ,

(ii) the constant, K , also appears to be the same in both glasses and is about $743 \pm 20 [\text{\AA} (\text{°C})^{1/2}]$.

(iii) the constant, T_0 , however, is significantly different for the two glasses; i.e., $T_0 = T_0(C_0)$.

For the glass without alumina T_0 is about $753.5 (\text{°C})$. For both glasses, the values of T_0 found are less than the respective coexistence temperatures, $T_p(C_0)$.

In preliminary efforts to explain these results, it was suggested that the measured $\lambda(T, C_0)$ is some temperature dependent characteristic length of the system and may be related to the correlation length, $\xi(T, C_0)$. The classical theories predict, for critical composition C_c ,

$$\xi(T, C_c) \approx (T - T_c)^{-\nu} \quad \nu = 0.50. \quad (2)$$

A reasonable extension of Eq. (2) to noncritical compositions is obtained by substituting for T_c in Eq. (2) the (so-called spinodal) temperature $T_{sp}(C_0)$, i.e.,

$$\xi(T, C_0) \approx [T - T_{Sp}(C_0)]^{-0.50} \quad (3)$$

[The spinodal temperature for a noncritical composition, C , defines the lower limit of metastability of a homogeneous system in the two phase region. For such a system, the Helmholtz free energy density $f(T, C)$, should be analytic in the entire T - C plane (including the critical point and the coexistence curve), and

$$\partial^2 f / \partial C^2 \Big|_{C_0, T_{Sp}(C_0)} = 0.]$$

Owing to the remarkable agreement of the values of exponent ν for the observed data [Eq. (1)] and classical theories [Eq. (3)], we assumed that

$$\chi(T, C_0) = \text{const. } \xi(T, C_0) \quad (4)$$

where the proportionality constant in Eq. (4) is temperature independent. Equation (4) implies that

$$T_0(C_0) = T_{Sp}(C_0). \quad (5)$$

The purpose of this work was to report an examination of the validity of Eq. (5). For this purpose an independent estimate of $T_{Sp}(C_0)$ from equilibrium measurements in the two phase region was obtained. In particular, the volume fraction of the minor phase at various temperatures in the two phase region was measured. The results agree with Eq. (5).

The propagation of sound waves near the critical point can be used to examine the effect of composition fluctuations of the diffusion coefficient. Longitudinal and shear ultrasonic measurements were conducted above the phase transition temperature of a soda borosilicate glass mixture. The distribution of volume relaxation times in the mixture was calculated from longitudinal and shear modulus measurements. The ultrasonic relaxation measurements allowed the investigation of two distinct effects in the distribution of relaxation times as the temperature was lowered toward the critical point. At high temperatures, a coupling between the compressional component of the ultrasonic wave and supercritical fluctuations in composition was observed as an anomalous broadening of the distribution of volume relaxation times. This interaction allowed a measure of the average composition fluctuation lifetimes, τ_D , as a function of temperature. At lower temperatures, as τ_D became longer than the volume relaxation times, the behavior of the distribution followed closely the predictions of an environmental relaxation model proposed by these authors for the analysis of shear relaxation processes in the same material.

The theoretical basis of the understanding of spinodal decomposition has largely come from the work of Hillert, Cahn, and Hillian in the past decade. Notable improvement to this early development has been made recently by Cook, who considered the effect of random thermal fluctuations (Analogous to Brownian motion) on the spinodal kinetics. His theory provides an explanation for the experimentally observed curvature in the $R(k)/k^2$ plot for two component systems, where $R(k)$ is the growth rate of composition fluctuation with wave vector k and $k = [k]$. However, Cook's theory predicts a common crossover point for all small-angle x-ray scattering (SAXS) curves which represent the early stages of the decomposition including the initial, "as quenched" state. A survey of the published SAXS data from various systems shows that the curves from as quenched samples do not intersect those corresponding to early stages of spinodal decomposition at this common point. This raises the question whether or not the occurrence of the crossover point is a necessary feature of the linear spinodal theory.

It was demonstrated from theoretical considerations that occurrence of a cross-over point (i.e., the critical wave vector for which the growth rate is zero) represents the onset of nonlinear stages in the spinodal growth, provided the initial conditions are such that prior decomposition has not occurred at some lower temperature. This conclusion was verified in a SAXS experiment on the B_2O_3 - PbO - Al_2O_3 .

In recent years, several studies have attempted to distinguish between two commonly accepted mechanisms of phase separation in glasses, namely, nucleation and growth (N&G) and spinodal decomposition (SD). The studies using light or small angle x-ray scattering can directly verify Gahn's spinodal decomposition theory which predicts the preferential growth of a selected band of Fourier components of the composition fluctuations in the scattering spectra. The prediction for N&G mechanism is quite different, in that no such selective growth is expected. Electron-microscope studies are based on the notion that while the N&G process produces initially isolated minor phase particles distributed randomly in the matrix phase (assuming no foreign surfaces exist in the melt), the SD produces an interconnected morphology in which both phases are connected over large distances in the sample. It is emphasized that these predictions are for early stages of the phase separation, and coarsening in later stages is expected to produce a break in the interconnectivity of the spinodal microstructure. On the other hand, interconnectivity in N&G microstructure can result by an intersecting growth mechanism as proposed by Haller. In view of these difficulties, the morphological method of distinguishing between the N&G and SD mechanism remains controversial.

Volume fraction of the minor phase in an alumina doped sodium borosilicate glass inside the immiscible region was studied. It was shown that such a study permits a distinction between the two mechanisms of phase separation, namely spinodal decomposition and nucleation and growth. For spinodal decomposition, the volume fraction decreases initially, whereas for nucleation and growth it increases with heat-treatment time.

Critical point theories have generally predicted that the diffusion coefficient vanishes at the transition temperature. Near the transition temperature of oxide glasses, we have observed large but finite increases in viscosity which are related to inverse of the diffusion coefficient. However, far below the transition temperature "anomalous" viscosity behavior should be expected due to the two-phase nature of the glass.

In this paper viscosity and electron microscopy measurements were reported on a phase separating glass as a function of time, at various temperatures. The viscosity changed by five orders of magnitude during the phase separation in a time period identified to be solely in the coarsening stage by electron microscopy. The stage during which composition changes are dominant occurs very quickly despite the high starting viscosity (10^{11} P) and, therefore, is nearly complete before reliable viscosity data can be obtained (2 min). Analysis of the rate of increase of the average particle size identified a rearrangement stage proceeding by bulk diffusion through the fluid phase with an apparent activation energy of 98 k/cal mole (4.1×10^5 J/mole). Superposition of the viscosity-microstructure size curves for various temperatures demonstrated that the change in viscosity was totally controlled by the growth of the viscous phase whose activation energy for viscosity is 132 k/cal mole (5.52×10^5 J/mole). The change of viscosity with time was explained in terms of changes in the size of the microstructure by applying an environmental relaxation model proposed by two of the authors.

Structural Relaxation and Viscoelasticity: The objective of this research was to arrive at an accurate empirical description of the kinetics of the variation of properties during structural relaxation, particularly in response to complicated pressure or temperature histories.

When a liquid is rate cooled or heated through the glass transition region, the onset of glass-like behavior, i.e., structural relaxation effects, is often characterized in terms of the glass transition temperature, T_g , which specifies roughly the temperature of the "break" in the property-temperature curve. It was known that the observed value of T_g for a glass depended on heating or cooling rate q . It was shown that this interdependence of T_g and q could yield information on the kinetic parameters controlling the structural relaxation, in particular that

$$d \ln |q| / d(1/T_g) \approx -\Delta h^*/R \quad (6)$$

where R is the ideal gas constant and Δh^* is the activation enthalpy for the relaxation times controlling the structural relaxation. The conditions necessary for the validity of this relaxation are that the structural relaxation be describable by a temperature-independent distribution of relaxation times and that the glass be cooled from a starting temperature well above the transition region and subsequently reheated at the same rate starting from a temperature well below the transition region. Experimental measurements of T_g vs. q were presented for As_2Se_3 , B_2O_3 , potassium silicate, and borosilicate crown glasses. Δh^* was found to be equal within experimental error to the activation enthalpy for the shear viscosity.

It is often not possible to measure T_g over a wide range of cooling or heating rates because of lack of sensitivity of the measuring instruments at low rates and the problem of temperature gradients at high rates. It was shown that by monitoring the variation of a property during heating at a convenient experimental rate after cooling through the glass transition region at a variety of rates q , the dependence of the limiting fictive temperature T_f' attained by the glass after rate cooling can be measured. It was shown by extending an earlier theory of Ritland to the case of a spectrum of relaxation times that the dependence of T_f' on cooling rate q is given by

$$d \ln |q| / d(1/T_f') \approx -\Delta h^*/R \quad (7)$$

Measurements of T_f' versus q for the property enthalpy H were carried out by differential scanning calorimetry for three glasses; typical results are shown for B_2O_3 glass in Fig. 3. The Δh^* values assessed via Eq. (7) were in good agreement with the shear viscosity activation enthalpies in the glass transition region.

The technique of digital correlation light scattering spectroscopy was applied to the measurement in an oxide glass ($0.5 Na_2O - 0.5 K_2O - 3 SiO_2$) of linear viscoelastic relaxation. Light is scattered in the liquid from index of refraction (and hence density) fluctuations. Since these fluctuations grow and decay via the structural relaxation process, correlation analysis of the time dependence of the intensity of the scattered light at several temperatures gives the linear relaxation kinetic parameters A , Δh^* and B for relaxation of longitudinal strain in response to longitudinal stress. Digital correlation spectroscopy allowed measurements of relaxation on time scales in the range 10^{-6} to 10^2 s, i.e., in the upper end of and somewhat above the glass transition region. This region is generally inaccessible by other relaxation techniques. As predicted, the temperature dependence of the longitudinal relaxation times measured by this technique agreed well with that of the shear viscosity.

The digital correlation spectroscopy technique was used to characterize linear viscoelastic relaxation in vitreous B_2O_3 over an extensive temperature range. It was found that the parameter, characterizing the distribution of relaxation times, was temperature dependent in regions where the shear viscosity activation enthalpy exhibited a temperature dependence. This supports models, which presumed that transport in highly viscous liquids is based on cooperative motion of regions of large size.

The $K_2O-B_2O_3$ system, along with other alkali borate systems, shows peculiar viscosity behavior. As K_2O is added to B_2O_3 , the viscosity isotherm passes first through a minimum and then through a maximum. Ultrasonic relaxation studies showed that the minimum and the maximum are due to the behavior of the most probable relaxation time and to the width of the distribution of relaxation times for longitudinal stress. These results support a model which accounts for the viscosity on the basis of the effect of the K_2O content on the relative numbers of BO_3 and BO_4 groups in the melt. The ultrasonic relaxation measurements show no indication of a previously suggested phase transition in this system.

Electrical Relaxation Phenomena: The dielectric constant ϵ' and electrical conductivity σ of a glass-forming 40 mol% $Ca(NO_3)_2$ -60 mol% KNO_3 melt were measured over a frequency range of 0.02 Hz-1 MHz and a temperature range of 25-96°. Measurements were carried out both on the equilibrium liquid above 60° and the nonequilibrium glass below 60°. This was the first time a thorough set of electrical relaxation measurements had been carried out on both glass and liquid.

The observed frequency dispersions in ϵ' and σ were attributed to a nonexponential decay of the electric field via the ionic diffusion process and analyzed as such. It was found that the electric field relaxation was well described by the decay function $\phi(t) = \exp[-(t/\tau_0)^\beta]$ · $0 < \beta \leq 1$. Typical results are shown in Fig. 5 for $M'(\omega)$ and $M''(\omega)$.

The mean electric field relaxation time, $\langle\tau_0\rangle$, for the liquid was found to be faster than the mean shear stress relaxation time, $\langle\tau_s\rangle$, by a factor ranging from 10 to 10^4 over the temperature range 96-60°, indicating a solid-like ionic conductivity mechanism in the highly viscous melt. The activation enthalpy for the electrical conductivity dropped from 78 kcal/mol for the equilibrium liquid to 24 kcal/mol for the glass. The difference between liquid and glass activation enthalpies was attributed to thermally induced structural changes in the equilibrium liquid. The width of the spectrum of electric field relaxation times was temperature independent for the glass but broadened with increasing temperature for the liquid. From this it was concluded that the source of the spectrum of relaxation times was the microscopic heterogeneity of the vitreous system and that the temperature dependence of the width of the spectrum for the liquid reflected thermally induced structural changes.

When one alkali is replaced by a second alkali in a network glass (e.g., glasses in the series $X Na_2O - (1-X)K_2O - 3 SiO_2$ with $0 \leq X \leq 1$) the ionic transport properties show striking departures from additivity. For example, the electrical conductivity at intermediate compositions passes through a minimum that may be as much as a factor 10^6 below the conductivity value predicted from additivity. Likewise in mixed alkali glasses there is observed a strong mechanical relaxation (relaxation of shear stress in response to applied shear strain) that is absent in the corresponding single alkali glasses. Previous investigators found a minimum in dielectric loss at temperatures and compositions where a strong mechanical relaxation peak is observed. They concluded that the mechanism responsible for the mixed alkali mechanical relaxation peak (possibly exchange of sites between, e.g., a Na^+ and a K^+ ion) was electrically inactive.

An investigation of both mechanical and electrical relaxation in a 0.5 Na₂O - 0.5 K₂O - 3 SiO₂ glass. Plots of the real part of the normalized mechanical modulus, N' , and of the normalized electrical modulus, $N'_{el} (= M'(\omega)/M_{00})$, versus a reduced frequency $\omega\tau_1$ show that the electrical relaxation curve lies at much higher frequencies than the mechanical relaxation curve. This means that the electric field decays much faster (perhaps via the diffusion of the more mobile cations) than does the mechanical stress field. Hence the mixed alkali mechanical peak does not have an observed electrical analog, not because the process responsible for the mechanical relaxation is inherently electrically inactive, but rather because the driving force (the electric field) vanishes inside the glass much faster than the mixed alkali process is capable of responding to it.

There was some question as to whether the mixed alkali effect was confined to properties associated with ionic transport or whether mixed alkali effects could be observed in equilibrium thermodynamic properties and in dynamic properties associated with rearrangement of the network, e.g., viscosity and structural relaxation. To partially answer this question, heat capacities of a series of mixed-alkali glasses of composition (in mol%) 24.4(Na₂O + K₂O) - 75.6 SiO₂ were measured in the transition region by differential scanning calorimetry. It was found that the glass heat capacities at 700K and the equilibrium liquid heat capacities were the same for all glasses on a per-g. atom basis and equal, respectively, to 5.6 ± 0.1 and 6.8 ± 0.1 cal/g.atom K. The glass transition temperatures exhibited negative deviations from additivity, but the heat capacity curves in the transition region of all the glasses for identical heating rates and thermal histories could be superimposed on the same reduced plot. This behavior indicated that the shape of the structural relaxation functions are the same for all the glasses. These results support the conclusion that there is no unique "mixed-alkali effect" on thermodynamic or structural relaxation properties and that the term should be reserved for properties relating to ionic transport.

AFOSR Program Manager: Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Basis for Liquid Crystal Field Effects
2. PRINCIPAL INVESTIGATOR: Dr. J. David. Margerum
Hughes Research Laboratories
Malibu, California 90265
3. INCLUSIVE DATES: 1 May 1972 - 30 June 1975
4. CONTRACT NUMBER: F44620-72-C-0075
5. COSTS AND FY SOURCE: \$40,503 FY72 \$45,986 FY75
20,057 FY73 46,346 FY76
29,988 FY74
6. SENIOR RESEARCH PERSONNEL: P. O. Braatz M. J. Little
A. Graube J. T. Marx
J. E. Jensen Dr. L. J. Miller
A. M. Lackner D. S. Smythe
Dr. H. S. Lim Dr. S. Y. Wong
7. JUNIOR RESEARCH PERSONNEL None
8. PUBLICATIONS:

"Improved DC Dynamic Scattering with Redox Dopants in Ester Liquid Crystals", H. S. Lim and J. D. Margerum, Appl. Phys. Lett. 28, 478-480 (1976).

"Dopant Effects on DC Dynamic Scattering in a Liquid Crystal: Microscopic Pattern Studies", H. S. Lim and J. D. Margerum, J. Electrochem. Soc. 123, 837-838 (1976).

"Electro-optical Applications of Liquid Crystals", J. D. Margerum and L. J. Miller, J. Colloid and Interface Sci. (in press, Vol. 58, 1977). This review also appears as a chapter in a book consisting of the Plenary and Invited lectures given at the 50th International Conference on Colloids and Surfaces in San Juan, Puerto, Rico, in June 1976.

"Effect of Dopants on the Conductivity Anisotropy and AC Dynamic Scattering of Liquid Crystals" J. D. Margerum, H. S. Lim, P. O. Braatz and A. M. Lackner, submitted to Mol. Cryst. Liq. Cryst.

"Alignment Effects on the Dynamic Scattering Characteristics of an Ester Liquid Crystal" M. J. Little, H. S. Lim and J. D. Margerum, submitted to Mol. Cryst. Liq. Cryst.

"Electrochemical Properties of Dopants and the DC Dynamic Scattering of a Nematic Liquid Crystal", H. S. Lim, J. D. Margerum and A. Graube, submitted to J. Electrochem. Soc.

"Molecular Bases for Liquid Crystal Field Effects" J. D. Margerum, Fin. Tech. Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program was to provide a better understanding of the molecular and ionic interactions in liquid crystal electrooptical effects. These studies on the electrochemical and structural effects of conductivity dopants on the mechanism of dynamic scattering in phenyl benzoate nematic liquid crystals have helped define major improvements in the performance characteristics and the operational lifetime of dynamic scattering displays. The following is a brief summary of these accomplishments:

Electrochemical studies in solvents showed that while liquid crystal compounds undergo irreversible oxidation and reduction reactions, redox dopants undergo reversible reactions at lower potentials. This is the basis of using these redox dopants in liquid crystals to improve the stability of dc dynamic scattering.

Studies of a redox dopant pair in nematic ester liquid crystals showed long-term operational lifetimes (two years of continuous operation at 20 V dc) for dc dynamic scattering in test cells. These dopants also improved performance by describing the dc threshold for scattering to $\sqrt{2}$ V and by giving scattering levels in the 10 to 20 V range.

The mechanism of dc dynamic scattering in an ester liquid crystal was shown to depend upon the structure of the dopants. Salts, electron donors and electron acceptors all showed different microscopic flow patterns. These results showed that unipolar charge injection and space charge flow occur with a single redox dopant (donor or acceptor) and that the dynamic scattering turbulence occurs mainly at the opposite electrode from the charge injection reaction.

The conductivity anisotropy of liquid crystals is shown to be highly dependent on the structure of the conductivity dopants as well as the structure of the liquid crystals to which they are added. The threshold voltage for ac dynamic scattering in a given liquid crystal decreases with increasing values of the conductivity anisotropy ratio ($\sigma_{\parallel}/\sigma_{\perp}$) in general agreement with the Carr-Helfrich theory. The optical density of scattering at 30 V rms is directly proportional to $\sigma_{\parallel}/\sigma_{\perp}$. Thus the dynamic scattering characteristics of a display cell are highly dependent upon the structure and conductivity anisotropy of the dopants.

The ac dynamic scattering threshold voltage, response times, and turbulent flow patterns are dependent on the surface alignment of the liquid crystal. The threshold voltage increases linearly with decreasing values of $\cos\bar{\theta}$, where $\bar{\theta}$ is the average tilt angle of the liquid crystal off the two electrode surfaces of a thin transparent cell. The response times are fastest for surface-parallel alignment ($\bar{\theta} = 0^\circ$). The scattering versus voltage curves indicate that surface-parallel alignment is best for gray scale displays with fast response times, while surface-perpendicular alignment ($\bar{\theta} = 90^\circ$) is best for two-level multiplexed displays with slow decay times.

AFOSR Program Manager: D. W. ELLIOTT

COMPLETED PROJECT SUMMARY

1. TITLE: The Reactivity and Structure of Solid Surfaces
2. PRINCIPAL INVESTIGATOR: Dr. Robert P. Merrill
Department of Chemical Engineering
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3. INCLUSIVE DATES: 1 November 1971 - 31 July 1975
4. CONTRACT NUMBER: AFOSR-72-2218
5. COSTS AND FY SOURCE: FY72 \$55,140; FY73 \$43,385; FY74 \$56,208; FY75 \$47,449
6. SENIOR RESEARCH PERSONNEL: Dr. Robert Ducros
Dr. Jean-Jacques Ehrhardt
Dr. Vincent Perrichon
7. JUNIOR RESEARCH PERSONNEL: Arthur J. Baumgartner
Hugh W. Gowdy
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Richard I. Masel
David R. Monroe
Robert J. Purtell
George A. Stoll, Jr.
Herbert H. Sawin
Kevin K. Tremper
Richard C. Vincent
W. Henry Weinberg
Ralph E. White
8. PUBLICATIONS:

"Crystal Field Surface Orbital-Bond Energy Order (CFSO-BEBO) Model for Chemisorption: Application to Hydrogen Adsorption on a Platinum (111) Surface", R. P. Merrill and W. H. Weinberg, Surface Science, 33, 493 (1972).

"The Scattering of Helium, Neon, Argon, Krypton, Xenon, and Deuterium from a Tungsten (110) Surface Characterized by LEED", R. P. Merrill and W. H. Weinberg, J. Chem. Phys. 56, 2881 (1972).

"Atomic and Molecular Diffraction and Scattering from a Tungsten Carbide Surface Characterized by LEED", W. H. Weinberg and R. P. Merrill, J. Chem. Phys. 46, 2893 (1972).

"Crystal Field Surface Orbital-Bond Order Bond Energy (CFSO-BEBO) Calculations of Adsorption: II. Carbon Monoxide, Oxygen and Carbon Dioxide on Platinum (111) and Oxygen on Nickel (111)", W.H. Weinberg and R. P. Merrill, Surface Science 39, 206 (1973).

"Residence Time Analysis of Rare Gas Atoms Trapped at a Solid Surface", W. H. Weinberg and R. P. Merrill, J. Vac. Sci. & Tech. 10, 411 (1973).

"The Scattering of Hydrogen, Deuterium, and the Rare Gases from Silver (111) Single Crystals", R. Sau and R. P. Merrill, Surface Science, 34, 268 (1973).

"Atomic and Molecular Scattering, Diffraction, and Trapping on Tungsten and Platinum Surfaces", in Adsorption-Desorption Phenomena, F. Ricca, ed., Academic Press, London & New York, 1972, p. 151.

"Atomic and Molecular Scattering from Crystallographically Well-defined Surfaces", R. P. Merrill, J. Vac. Sci & Tech. **9**, 803 (1972).

"The Structure and Chemistry of Ethylene Adsorbed on Platinum (111) -- CFSO-BEBO Calculations and Experimental Studies", W. H. Weinberg, H. A. Deans and R. P. Merrill, Surface Science **41**, 312 (1974).

"Rainbow Scattering from a Strongly Periodic Metal Surface", A. G. Stoll and R. P. Merrill, Surface Science, **40**, 405 (1973).

comment on "Scattering of Monoenergetic Argon Beams from Heated Platinum: Out-of-place Time-of flight Measurements", R. P. Merrill, Surface Science **40**, 715 (1973).

"Semiclassical Trajectory Calculations of Helium Scattering from W(112) Surfaces", R. I. Masel, W. H. Miller and R. P. Merrill, Surface Science **46**, 681 (1974).

"Concentration Profiles in Impregnation of Porous Catalysts", R. C. Vincent and R. P. Merrill, J. Catalysis **35**, 206 (1974).

"Scattering of Helium and Deuterium from Single Crystal Pt(111) Compared from Two Different Laboratories", S. Bernasek, G. A. Somorjai and R. P. Merrill, J. Vac. Sci. & Tech., **12**, 655 (1975).

"Scattering of Light Atoms from Strongly Periodic Surfaces", A. G. Stoll, Jr., R. E. White, J. J. Ehrhardt, R. I. Masel and R. P. Merrill, J. Vac. Sci & Tech. **12**, 192 (1975).

"A Semiclassical Model for Atomic Scattering from Solid Surfaces: He and Ne Scattering from W(112)", R. I. Masel, R. P. Merrill and W. H. Miller, Accepted for publication in J. Chem. Phys., 15 Jan 1976.

"Scattering of Argon and Neon from W(112)", R. E. White, J. J. Ehrhardt and R. P. Merrill. Accepted for publication in J. Chem. Phys., 15 Jan 1976.

"Helium Diffraction from Tungsten (112)", A. G. Stoll, Jr., J. J. Ehrhardt and R. P. Merrill. Accepted for publication in J. Chem. Phys., 15 Jan 1976.

"Crystal Field Surface Orbital-Bond Energy Bond Order (CFSO-BEBO) Calculations for Surface Reactions: I. The Reactions $\text{CO} + \text{O}_2$, $\text{NO} + \text{CO}$, and $\text{H}_2 + \text{O}_2$ on a Platinum (111) Surface", W. H. Weinberg and R. P. Merrill. Accepted for publication in J. Catalysis.

"Quantum Scattering from a Sinusoidal Hard-wall: Atomic Diffraction from Solid Surfaces", R. I. Masel, R. P. Merrill and W. H. Miller. Accepted for publication in Physical Review, 15 December 1975.

"Semiclassical Theories and Quantum Hardwall Calculations of Atom Surface Scattering", R. I. Masel, R. P. Merrill and W. H. Miller, J. Vac. Sci & Tech. Jan-Feb (1976).

"Atomic He Diffraction and LEED Studies of Oxygen Adsorbed on W(112)", J. J. Ehrhardt and R. P. Merrill. Accepted for publication in Surface Science.

"The Interaction of Oxygen with Pt (110)", R. Ducros and R. P. Merrill. Accepted for publication in Surface Science.

"Oxygen Adsorption on Pt(111) Using a Molecular Beam", A. G. Stoll Jr., and R. P. Merrill. Submitted to Surface Science.

"A Study of the Catalytic Properties of Iridium Using a Current Probe Field Emission Microscope", H. W. Gowdy, PhD. Thesis, 1972.

"A Study of Carbon Monoxide Adsorption on Single Planes of Iridium Using a Current-probe Field Emission Microscope", K. K. Tremper, M. S. Thesis, 1973.

"Concentration Profiles in Impregnation of Porous Catalysts", R. C. Vincent, M. S. Thesis, 1974.

"Argon and Neon Scattering from W(112): Surface Rainbows", R. E. White, M. S. Thesis, 1973.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research continues the effort begun within the background of a resurging interest in atomic and molecular beam scattering and the development of a host of new surface spectroscopies. The emphasis of the atomic scattering has been on developing atomic helium scattering as a tool for investigating surface structure and atomic morphology. The chemical systematics has emphasized the interaction of oxygen with noble metals and the role of adsorbed oxygen in oxidation catalysis and corrosive oxidation. LEED, Auger Spectroscopy, and programmed desorption have been the principal experimental techniques which have been used in addition to the atomic scattering. Theoretical studies applying semiclassical theory to atomic scattering has been singularly successful and molecular orbital techniques are being applied in a limited way to some chemisorption problems. A small effort has also been directed toward understanding imbibition of liquids in porous media in order to systematize catalyst impregnation techniques. This work seems applicable also to some key problems in monopropellant catalyst stability.

The scattering of the rare gases from Ag(111) demonstrated that adsorption of background gases was negligible on silver and established that helium scattering could be used as a tool to characterize, qualitatively, the state of a silver scattering target. This has permitted useful scattering measurements in many laboratories without LEED and Auger within the scattering chamber. The silver scattering also fits with the phenomenological identification of scattering within the three regimes, quasi-elastic, inelastic, and trapping dominated, and established the well depth reduced by the beam energy as the dominant scattering parameter. Work with polyatomic molecules on Pt(111) showed this parameter to be more important than internal molecular structure or the surface to gas atomic mass ratio. Theoretical analysis of expected residence times for molecule initially trapped at solid surfaces but not thermally accommodated gave appropriate correction to the square-well trapping theory developed earlier.

Rare gas scattering from W(112), a ridge-trough structured surface, showed well-resolved diffraction for helium scattering and rainbow patterns for neon. Only uni-lobular scattering was observed for argon and the heavier rare gases. Application of semiclassical scattering theory to these experiments reveals a scattering pattern which can be envisioned as a product of the classical scattering envelope, an inter-cellular interference function or "structure" factor, and a series of δ functions which give the Laue diffraction conditions. The classical part gives the rainbow pattern which is observed (neon) when the broadening induced by the energy spread in the incident beam is large compared to the separation between diffraction features. When beams are more broadly spaced, each beam within the rainbow angles is resolved, but is modulated by the classical envelope. Application of this analysis to the W(112) surfaces has shown that the helium scattering cross-section for tungsten atoms is approximately double the cross-section deduced from the crystal radius and the repulsive wall is much "softer" than that deduced for lithium fluoride.

Helium scattering from an oxygen-covered W(112) surface with a (1x2) diffraction pattern has demonstrated the utility of atomic diffraction for studying adsorbed monolayers and demonstrated that the W(112) - (1x2) is surface reconstruction rather than the subsurface reconstruction that others have suggested from only LEED studies.

The observed chemical systematics of ethylene adsorption, dissociation, and thermal decomposition on Pt(111) have been essentially reproduced by CFSO-BEBO calculations and EHMO and CNDO calculations of atomic hydrogen adsorption on beryllium clusters have been compared to ab initio calculations. Not surprisingly the EHMO are found to be inadequate even to give the correct qualitative behavior for this system.

Adsorption of oxygen has been found to be slightly activated on Pt(111) but not activated on Pt(110). The resulting adsorbed oxygen (believed to be atomically adsorbed) reacts with near unity reaction probability with hydrogen and/or carbon monoxide which is independent of the oxygen coverage down to 1-5% of a monolayer. On Pt(110) an epitaxial surface oxide nucleates at temperatures above 700°C which appears to be platinum oxide and is stable up to 1000°C. The surface chemistry of the low temperature, chemisorbed oxygen can account qualitatively for the observed rates of oxidation catalysis in auto exhaust mufflers. These high rates are also present in hydrazine decomposition on monopropellant iridium catalysts and similar studies on single crystals might also yield the controlling catalytic kinetics.

AFOSR Program Manager: R. W. Haffner, Lt Col

COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemical Studies in Aluminum Chloride Melts.

2. PRINCIPAL INVESTIGATOR: Dr. R. A. Osteryoung
Department of Chemistry
Colorado State University
Ft. Collins, Colorado 80523

3. INCLUSIVE DATES: 1 March 1975 - 31 May 1976

4. GRANT NUMBER: AFOSR-75-2776

5. COST AND FY SOURCE: \$35,100 FY75

6. SENIOR RESEARCH PERSONNEL: Dr. J. Phillips
Dr. R. Gale

7. JUNIOR RESEARCH PERSONNEL: J. Robinson

8. PUBLICATIONS:

"Electrochemical Studies of Mo-Species in AlCl_3 -NaCl Solvent Systems", J. Phillips and R. A. Osteryoung, submitted to J. Am. Chem. Soc., or J. Electrochem. Soc.

"Acid-Base Chemistry of Chalcogenides in Sodium Tetrachloroaluminate Melts", in prep for J. Am. Chem. Soc.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research program involved fundamental studies of the reactions between metal and nonmetal electrodes and non-aqueous molten salt electrolytes. Such systems have been shown to have the potential of providing higher energy cells than are possible in the more conventional aqueous systems. The acid-dependent chemistry of sulfur was investigated. The Nernst behavior of the S/S^{2-} couple was in accord with $\text{S}_2 + 4\text{e} = 2\text{S}^{2-}$ and the acid-base dependence can be expressed as $\text{S}^{2-} + \text{AlCl}_4^- \rightleftharpoons \text{AlSCl}_2 + 3\text{Cl}^-$. This explains the solubilization of metal sulfides in acid-chloroaluminate systems. Oxides, selenides and tellurides show much the same behavior as sulfides. The stoichiometry indicates that the neutralization reaction for these bases may be written $\text{x}^{2-} + 3\text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{AlXCl} + 5\text{AlCl}_4^-$ where X is S, O, Se or Te. A detailed electrochemical study of selenium was undertaken. The following mechanism can be proposed: $\text{Se} + 3\text{Cl}^- \rightleftharpoons \text{SeCl}_3^- + 2\text{e}^-$; $\text{SeCl}_3^- + 2\text{Cl}^- \rightleftharpoons \text{SeCl}_5^- + 2\text{e}^-$.

Selenium also appears to exist, as determined potentiometrically, as a dimer. The electrochemistry of various molybdenum species was studied. Mo(V) reacts to form Mo(III) which is further reduced to Mo(II) and Mo(0) . The last two steps involve considerable surface chemistry. A mechanism is postulated to explain the $\text{Mo(V)} + 2\text{e}^- \rightleftharpoons \text{Mo(III)}$ electrode process.

AFOSR Program Manager: Mr. D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemistry of Hydrazine-Hydrazine Azide Mixtures
2. PRINCIPAL INVESTIGATOR: Dr. Charles T. Brown
United Technologies Research Center
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 1 March 1972 - 30 June 1976
4. GRANT NUMBER: AFOSR-72-0049
5. COSTS AND FISCAL YEAR SOURCE: \$38,579 FY72; \$19,960 FY73; \$32,392 FY74;
\$41,501 FY75; \$42,987 FY76
6. SENIOR RESEARCH PERSONNEL: Mr. Sid Russell
7. JUNIOR RESEARCH PERSONNEL: Ms. Patricia DeFelice
Mr. John Dannecker
Mr. Terry Fondrk

8. PUBLICATIONS:

"The Preparation of Purified Hydrazine", C. T. Brown, to be submitted to The Journal of Chemical and Engineering Data.

"The Cathodic Process in Anhydrous Hydrazine", C. T. Brown. To be submitted to The Journal of the Electrochemical Society.

"Electrical Conductivity Studies of Hydrazine-Water and Hydrazine-Carbon Dioxide Mixtures", C. T. Brown. To be submitted to The Journal of the Electrochemical Society.

"The Electrochemistry of Hydrazine-Hydrazine Azide Mixtures", presented at the University of Poitiers, Poitiers, France, in October 1974, as part of an International Conference on "The Properties of Hydrazine and its Potential Applications as an Energy Source".

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

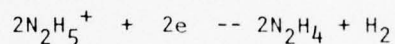
The experimental program was designed to examine hydrazine and hydrazine-derivatives as solvents for various electrolytes. In principle such solvent/solute mixtures could permit a wide range of electrochemical reactions which cannot be achieved in aqueous solutions. Hydrazine azide as a electrochemically active solute was selected because of the high theoretical oxidation potential for the azide ion. The kinetics of more conventional metal-metal ion couples were also investigated.

The effect of impurities on the electrochemical properties of hydrazine was investigated using as-received and specially purified samples. A purification procedure was developed which consisted of drying over CaH_2 followed by vacuum distillation. This procedure resulted in hydrazine with 0.05 percent water and less than 10 ppm CO_2 .

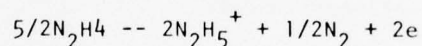
Conductivity measurements were used to characterize the effects of water, carbon dioxide and aniline (the three major impurities in hydrazine) on the electrochemical properties of hydrazine. Aniline had no effect on conductivity. The conductivity as a function of water content was found to obey the Onsager relationship for water concentrations up to 1.0 percent provided the hydrolysis reaction with hydrazine was taken into account. Above 1.0 percent water ionic association is evident and the effect of water on the ionic nature of hydrazine is minimized. Thus elaborate purification procedures are not necessary in order to use hydrazine as a solvent.

The effect of carbon dioxide on the conductivity of hydrazine was complex. It appears that both carbazic acid and ammonium carbonate are formed. It has been found that exposure of hydrazine to air must be minimized in order to maintain a carbon dioxide concentration on the order of 10 ppm. Proper control of the impurity levels resulted in hydrazine samples that could be used in electrode polarization studies without encountering interfering reactions.

Electrode polarization studies on platinum in hydrazine indicated a total potential range of about 1.2 volts without hydrazine decomposition. The cathodic reaction is diffusion controlled and proceeds according to:



The anodic reaction is activation controlled and proceeds according to:



Polarization experiments using hydrazine azide as a solute merely increased the conductivity of the system. There was no evidence of azide ion discharge. These experiments were repeated using monomethylhydrazine as a solvent. The cathodic process was the same as in hydrazine. In the absence of a supporting electrolyte it was possible to obtain a total potential range of ± 3 volts. In the presence of solutes (including hydrazine azide) the cathodic overpotential was the same as in hydrazine, but there was no evidence of nitrogen evolution at overpotentials as high as +4V (i.e., no azide in activity).

Studies of a variety of metal-metal ion couples in hydrazine indicate that aluminum and magnesium have high overpotentials for solvent decomposition and low overpotentials for the metal-metal salt couple. The aluminum electrode does not appear to be reversible, but the magnesium-magnesium chloride system indicates high reversibility at low overpotentials.

The results suggest that a research program should be conducted in which selected metal-metal ion and metal-insoluble metal salt couples would be investigated as a function of solvent composition and solute concentration in terms of high open-circuit potentials and low overpotentials. The solvent studies have been brought to the point where the solvent-electrode interactions are well understood, and the specific electrode processes can be studied without problems associated with the solvent.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Experimental and Theoretical Studies in Photochemistry
2. PRINCIPAL INVESTIGATOR: Stuart A. Rice
3. INCLUSIVE DATES: 1 September 1972 to 31 August 1976
4. CONTRACT NUMBER: AFOSR 44620-73-C-0005
5. COSTS AND FY SOURCE: \$118,317 FY73; \$112,550 FY74; \$115,832 FY75;
\$100,000 FY76; \$22,582 FY77
6. SENIOR RESEARCH PERSONNEL:

E. Dorko	J. Kushick
R. M. Gavin, Jr.	Y. T. Lee
E. Heller	K. J. S. Nordholm
K. Kay	N. C. Yang
7. JUNIOR RESEARCH PERSONNEL:

R. V. Carr	E. Li
K. Evans	J. Parson
D. Heller	R. B. Weisman
8. PUBLICATIONS:

"A Study of Primary Photochemical and Photophysical Processes in Chloro-and-Bromoacetylene" S. A. Rice, K. Evans, R. Scheps and D. Heller, Faraday Soc. 11, 69, 856 (1973).

"Spectroscopic Properties of Polyenes I. The Lowest Energy Allowed Singlet-Singlet Transition for Cis and Trans-1,3,5-Hexatriene". S. A. Rice, R. M. Gavin, Jr., and S. Risemberg, J. Chem. Phys. 58, 3160 (1973).

"Substitution Reactions of Fluorine Atoms with Unsaturated Hydrocarbons: Crossed Molecular Beam Studies of Unimolecular Decomposition". S. A. Rice, J. M. Parson, K. Shobatake and Y. T. Lee, Disc. Far. Soc. 55, 344 (1973).

"Unimolecular Decomposition of the Long-Lived Complex Formed in the Reaction $F+C_4H_8$ ". S. A. Rice, J. M. Parson, K. Shobatake and Y. T. Lee, J. Chem. Phys. 59, 1402 (1973).

"The Unimolecular Decomposition of Long-Lived Complexes of Fluorine and Substituted Mono-Olefins, Cyclic Olefins and Dienes". S. A. Rice, K. Shobatake, Y. T. Lee and J. M. Parson, J. Chem. Phys. 59, 1416 (1973).

"The Laboratory Angular Dependence and the Recoil Energy Spectrum of the Products of the Reaction $F + C_6D_6 \rightarrow D + C_6D_5F$ ". S. A. Rice, K. Shobatake, J. M. Parson, and Y. T. Lee, J. Chem. Phys. 59, 1427 (1973).

"The Reactions of F Atoms and Aromatic and Heterocyclic Molecules: Energy Distribution in the Reaction Complex". S. A. Rice, K. Shobatake and Y. Lee, J. Chem. Phys. 59, 1435 (1973).

"Intramolecular Vibrational Energy Transfer: A Study of Representations". S. A. Rice, K. G. Kay, J. Chem. Phys. 58, 4852 (1973).

"Decay of Fluorescence from Single Vibronic Levels of SO_2 ". S. A. Rice, M. H. Hui, Chem. Phys. Lett. 20, 411 (1973).

"An ITFITS Model for Vibration-Translation Energy Partitioning in Atom-Polyatomic Molecule Collision", S. A. Rice, K. Shobatake and Y. T. Lee, J. Chem. Phys. 59, 2483 (1973).

"A Crossed Molecular Beams Study of the Reaction $F + C_2H_2Cl_2 \rightarrow Cl + C_2H_2ClF$ ". S. A. Rice, K. Shobatake and Y. T. Lee, J. Chem. Phys. **59**, 6104 (1973).

"Influence of Large Amplitude Vibrational Motion on the Rate of Intersystem Crossing: A Study of Single Vibronic Level Fluorescence From Aniline- h_7 , Aniline-N, N- d_2 and Aniline- d_5 ". S. A. Rice, R. Scheps and D. Florida., J. Chem. Phys. **61**, 1730 (1974).

"Comments on the Dynamics of Primary Photochemical Processes". In Advances in Electronic Excitation and Relaxation, Vol II, edited by E. C. Lim (Academic Press, New York) pp. 111-320 (1975).

"Comments on the Spectrum and Photophysical Properties of Trimethylene-Cyclopropane". S. A. Rice, E. A. Dorko and R. Scheps, J. Phys. Chem. **78**, 568 (1974).

"Quantum Ergodicity and Vibrational Relaxation in Isolated Molecules". S. A. Rice, K. Sture J. Nordholm, J. Chem. Phys. **61**, 203 (1974).

"Intramolecular Energy Transfer in Cis-Trans Isomerization: A Study of Fluorescence from Single Vibronic Levels of Styrene", trans- Styrene- d , Styrene- d_8 , and Ethynlbenzene. S. A. Rice, M. H. Hui, J. Chem. Phys. **61**, 833 (1974).

"Nonradiative Processes in $p\text{-C}_6\text{H}_4\text{F}_2$ and $m\text{-C}_6\text{H}_4\text{F}_2$ ", S. A. Rice, C. Guttman, J. Chem. Phys. **61**, 661 (1974).

"Fluorescence Lifetimes of Individual Vibronic Levels of Partially Deuterated Benzenes: A Further Test of the Theory of Radiationless Processes", S. A. Rice, C. Guttman, J. Chem. Phys. **61**, 651, (1974).

"2,3-Naphtho-2,5-bicyclo(2.20) hexadiene". S. A. Rice, N. C. Yang, R. V. Carr, E. Li, J. K. McVey. J. A. C. S. **96**, 2297 (1974).

"Random Coupling Model for Molecular Dissociation" S.A. Rice, E. J. Heller, J. Chem. Phys. **61**, 936 (1974).

"Quantum Ergodicity and Vibrational Relaxation in Isolated Molecules II-Independent Effects and Relaxation to the Asymptotic Limit", S. A. Rice, S. Nordholm, J. Chem. Phys. **61**, 768 (1974).

"A Quantum Ergodic Theory Approach to Unimolecular Fragmentation", S. A. Rice, S. Nordholm, J. Chem. Phys. **62**, 157 (1975).

"Stablization of a Mode-Locked Nd: Glass Laser by Intracavity Second-Harmonic Generation", S. A. Rice, R. B. Weisman, Spectroscopy Ltrs, **8**(5) 329 (1975).

"Angular Momentum Conservation in Photochemical Fragmentation: A Simple Model", S. A. Rice, D. Florida, Chem. Phys. Ltrs, **33**, 207 (1975).

"Nonlinear Resonance and Stochasticity in Intramolecular Energy Exchange", S. A. Rice, D. W. Oxtoby, J. Chem. Phys. (submitted).

"Tunable Infrared Ultrashort Pulses from a Mode-Locked Parametric Oscillator", S. A. Rice, R. B. Weisman. submitted to Optics Communications.

"Reactions Induced by Incoherent Multiphoton Absorption", S. A. Rice, J. Jortner, to be submitted to J. Chem. Phys.

Papers by Postdoctoral Research Associate Eric J. Heller:

"Time Dependent Approach to Semiclassical Dynamics", J. Chem. Phys. **62**, 1544 (1975).

"Variational Correction to Wigner R-Matrix Theory of Scattering", D. J. Zviljac and J. C. Light, J. Phys. B: Atom. Molec. Phys. **8**, 1016 (1975).

"Wavepacket Path Integral Formulation of Semiclassical Dynamics", Chem. Phys. Ltrs. **34**, 321 (1975).

"Theory of J-Matrix Green's Functions with Applications to Atomic Polarizability and Phase Shift Error Bounds, Phys. Rev. A. **12**, 1222 (1975).

"Experimental and Theoretical Studies in Photochemistry", S. A. Rice, Fin. Tech. Rpt.

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The goal of the research is the elucidation of the primary physical and chemical processes following photo-excitation of a molecule. A variety of approaches has been used, all addressed to answering one or more of the following questions:

- (1) What general principles determine the nature of the primary products of a photochemical reaction?
- (2) How does the excitation process, e.g., the initial state selected, the use of coherent versus incoherent light, etc., influence the reaction products?
- (3) Does internal energy transfer compete with bond-breaking or isomerization? When and under what conditions is this important?
- (4) Can reaction pathways be selected or optimized by controlled excitation of selected initial states?

For several years before the contract period under discussion, the principal investigator participated in the development of a general theory of radiationless processes and initiated the application of that theory to photochemical reactions. The central theme of the theory is deceptively simple, namely that an initially prepared state of a molecule is, in general, nonstationary. The kind of nonstationary state prepared depends both on details of the molecular spectrum of states and on the nature of the excitation. The evolution of the prepared nonstationary state, which determines the nature of the reaction, is also influenced by the character of the spectrum of the molecule, the intramolecular couplings and rates of relaxation, the absence or presence of collisions, etc. Reduction of the general theory by application to specific problems has been one of the principle activities during the contract period. There has been fruitful exchange of insights as the theory and the experimental work developed side by side. Practical application of the findings of this research will depend on whether or not one can learn to control the coupled excitation and evolution of nonstationary molecular states and thereby develop a selective photochemistry.

Given the participation in the development of the general theory of radiationless processes, it was natural this research plays a role in testing that theory. Because of the influence of the initial state on the rate emphasized in the theoretical analysis, attention was focussed on determining the roles of the extent of vibrational excitation, amplitude, frequency and origin shifts,

and symmetry, for a typical radiationless process. The method selected, nano-second time resolved single vibronic level fluorescence spectroscopy, has also been used to study some photochemical reactions. That this is possible is testimony to the value of information obtained for photophysical radiationless processes, and the transferability of concepts for the description of photochemical reactions. A rather extensive test of the theory, for the case of intersystem crossing, has been completed, using as test cases benzene, several partially deuterated benzenes, aniline and deuterated anilines, and others. These investigations confirm many of the predictions of the general theory, and the utility of algorithms developed by Karl Freed.

Having studied radiationless processes in isolated molecules (on a time scale shorter than the time between collisions) it is natural to use the information obtained to learn how collisions lead to intramolecular energy exchange. Such processes are of great importance in unimolecular reactions, both those which are thermally induced and those induced by multiphoton absorption and putatively of use for isotope separation. As one example, was the development of a theory of laser induced photochemical reaction for the case of incoherent excitation. This class of reactions has just been discovered and reported by Grunwald (D. F. Dever and E. Grunwald, J. Am. Chem. Soc., 98, 5055 (1976)).

The first stage in the present studies of photochemical primary processes consisted of developing extensions of the theory with respect to the influence of changes in molecular geometry and the distribution of internal coupling strengths. Simultaneously, the application of the theory of radiationless processes to various photochemical reactions led to the study of intramolecular vibrational relaxation in an isolated molecule. As a result of work in Chicago and elsewhere, it is now apparent that this kind of relaxation can be slower than reaction in a number of cases, a finding likely to be of profound importance for the development of practical selective photochemistry. For, selectivity in a photochemical reaction will depend upon memory effects, that is, on being able to use a specific prepared vibronic state to produce specific reaction products. If intramolecular energy exchange is rapid so that the excitation energy placed in a molecule is scrambled rapidly, product selectivity is unlikely to occur. If, on the other hand, intramolecular energy exchange is slow, it is in principle possible (though not necessarily easy or efficient) to produce both different yields and different products by selective excitation of different initial states.

The theoretical contributions to this problem which have been made largely focus on the analysis of the behavior of simple models of dynamical processes. The studies completed to date confirm, on the whole, that it is possible that intramolecular energy exchange can be slow, but as of this writing the theory is very incomplete and has not yet yielded detailed understanding of when and why intramolecular energy exchange is fast or slow.

AFOSR Program Manager: J. T. Viola, Lt. Col.

COMPLETED PROJECT SUMMARY

1. TITLE: High Energy Chemical Reactivity
2. PRINCIPAL INVESTIGATOR: John Root
Department of Chemistry
University of California
Davis, California
3. INCLUSIVE DATE: 15 October 1972 - 31 December 1975
4. GRANT NUMBER: AFOSR-73-2460
5. COST AND FY SOURCE: \$44,158 FY73; \$35,000 FY74; \$34,997 FY75
6. SENIOR RESEARCH PERSONNEL: Dr. C. W. Tsao
Dr. R. P. Pettijohn
Mr. J. E. Harrison
7. JUNIOR RESEARCH PERSONNEL: Mr. F. E. Little
Mr. G. W. Mutch

8. PUBLICATIONS:

"Chemically Activated $^{14}\text{CH}_3\text{CF}_3$ from Cross Combination of ^{14}CH with CF_3 . An introductory Experimental Study", R. P. Pettijohn, G. W. Mutch, and J. W. Root, J. Phys. Chem., **79**, 2077 (1975).

"Details of Radiogaschromatography Apparatus", R. R. Pettijohn, G. W. Mutch, and J. W. Root, Microfilm Supplement to Ref 1.

"Chemically Activated $^{14}\text{CH}_3\text{CF}_3$ from Cross Combination of $^{14}\text{CH}_3$ with CF_3 . II. Collisional Energy Transfer to Fluorinated Ethanes". R. R. Pettijohn, G. W. Mutch, and J. W. Root, J. Phys. Chem., **79**, 1747 (1975).

"Details Concerning 6-Channel Solid-State Buffered Memory Scaler", R. R. Pettijohn, L. L. Lucas, and J. W. Root, AFOSR Technical Report, U. C. Davis, 1975.

"High Energy Chemical Reactivity", J. W. Root, Fin Tech Rpt.

9. ABSTRACT OF OBJECTIVE AND ACCOMPLISHMENT:

Experimental measurements have been made of gas-liquid critical constants for C_2H_6 and all the fluoroethane isomers. The semi-empirical molecular size analysis described previously appears to be applicable to virtually all substances, possibly excepting the low-temperature quantum fluids. However, based upon the limited amount of available data, anomalous behavior was indicated for the fluoroethanes. An experimental investigation of these substances was initiated in the hope of developing an independent validity test for the revised corresponding states analysis.

Experimental results substantiated the unusual excluded volume behavior of fluorinated ethanes and further showed a marked dependence of the critical temperature upon isomer structure, which was unusually large for organic substances. A straightforward explanation of this T_c behavior followed from the analysis of dipole-dipole and dipole-induced-dipole interactions for these substances.

Some degree of corroboration was sought for the corresponding states analysis, which seemed both too simple and too successful to be readily believable. However, the fluoroethane study actually compounded this credibility problem by demonstrating that not only the length parameter but also the well-depth molecular force constant could be reliably predicted from simple corresponding states assumptions.

A second major success followed from the continuation of the $^{14}\text{CH}_3\text{CF}_3$ unimolecular kinetics research which was initiated as AFOSR-68-1493.

Experiments at very low pressure revealed that the radiotracer technique provided heretofore unattainable sensitivity for unimolecular collisional energy transfer experiments.

Unimolecular kinetics is an established discipline with an immense literature and many eminent authorities, both in the U. S. and abroad. The theory is sufficiently challenging that few researchers undertake this type of research apart from individuals receiving graduate or post-graduate training in it. We were thus surprised to be in the apparent position of having developed a technique surpassing the capability of the best previous technology.

AFOSR Program Manager: J. T. Viola, Lt Colonel

COMPLETED PROJECT SUMMARY

1. TITLE: Highly Halogenated Organic and Organometallic Materials and Strained Ring Organometallics

2. PRINCIPAL INVESTIGATOR: Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

3. INCLUSIVE DATES: 1 October 1971 - 31 August 1975

4. GRANT NUMBER: AFOSR-72-2204

5. COSTS AND FY SOURCE: \$57,335 FY72; \$61,594 FY73; \$54,000 FY74; \$49,500 FY75

6. SENIOR RESEARCH PERSONNEL: Dr. M. Massol
Dr. B. Mauzé
Dr. Y. -M. Cheng

7. JUNIOR RESEARCH PERSONNEL: R. L. Lambert, Jr. G. J. Murphy
S. P. Hopper D. Daganí
H. Shih D. C. Annarelli
C. K. Haas J. L. Lefferts
R. A. Woodruff R. E. Mammarella
Y. M. Cheng D. F. Duncan

8. PUBLICATIONS:

"New Reactions of Phenyl(trihalomethyl)mercury Compounds. Dihalocarbene Addition to Azodicarboxylate Esters", D. Seyferth and H. Shih, J. Amer. Chem. Soc., **94**, 2508 (1972).

"Halomethyl-Metal Compounds. LI. An Improved Synthesis of α -Iodoalkyl Derivatives of Tin and Mercury by the Organozinc Route. Bis [(trimethylsilyl)iodomethyl]mercury", D. Seyferth, S. B. Andrews and R. L. Lambert, Jr., J. Organometal. Chem., **37**, 69 (1972).

"Halomethyl-Metal Compounds. LII. The Application of Phenyl(bromodichloromethyl)mercury, Phenyl(dibromochloromethyl)mercury and Phenyl(tribromomethyl)mercury as Dihalocarbene Sources at Room Temperature", D. Seyferth and H. Shih, Organometal. Chem. Synth., **1**, 415 (1972).

"Halomethyl-Metal Compounds. LIII. Reactions of Phenyl(trihalomethyl)mercury Compounds with Thiocarbonyl Derivatives", D. Seyferth, W. Tronich, R. S. Marmor and W. E. Smith, J. Org. Chem., **37**, 1537 (1972).

"A Convenient Organomercury CH_2 Transfer System", D. Seyferth and C. K. Haas, J. Organometal. Chem., **39**, C41² (1972).

"The Generation of Fluorocarboethoxycarbene by the Organomercury Procedure", D. Seyferth and R. A. Woodruff, J. Fluorine Chem., **2**, 214 (1972).

"Halomethyl-Metal Compounds. LIV. Phenyl(dihalocarbomethoxymethyl)mercury Compounds as Halocarbomethoxycarbene Transfer Agents", D. Seyferth, R. A. Woodruff, D. C. Mueller and R. L. Lambert, Jr., J. Organometal. Chem., **43**, 55 (1972).

"Crystal Structure of Methyl 5-Bromo-2-oxo- Δ^2 -1,3,4-oxadiazolin-3-carboxylate", D. Seyferth, H. Shih and M. D. LaPrade, J. Chem. Soc., Commun., 1036 (1972).

"Halomethyl-Metal Compounds. LV. The Synthesis of Phenyl(trifluoromethyl)mercury by Fluorination of Phenyl(tribromomethyl)-mercury", D. Seyferth and S. P. Hopper, J. Organometal. Chem., **44**, 97 (1972).

"Halomethyl-Metal Compounds. LVI. Trimethyltindihalomethyl lithium Reagents", D. Seyferth, F. M. Ambrecht, Jr., R. L. Lambert, Jr., and W. Tronich, J. Organometal. Chem., **44**, 299 (1972).

"Halomethyl-Metal Compounds. LVIII. The Insertion of Phenyl(bromo-dichloromethyl)mercury-derived Dichlorocarbene into C-H Bonds. Further Studies of the β - Metal Activated C-H Insertion Reaction", D. Seyferth, Y. M. Cheng and D. D. Traficante, J. Organometal. Chem., **46**, 9 (1972).

"Cyclohexyl(trihalomethyl)mercury Compounds. Very Reactive Dihalocarbene Precursors", D. Seyferth and C. K. Haas, J. Organometal. Chem., **46**, C33 (1972).

"Halomethyl-Metal Compounds. LVII. A Convenient Synthesis of Aryl(trifluoromethyl)mercury Compounds", D. Seyferth, S. P. Hopper and G. J. Murphy, J. Organometal. Chem., **46**, 201 (1972).

"Halomethyl-Metal Compounds. LX. Phenyl(trifluoromethyl)mercury, A Useful Difluorocarbene Transfer Agent", D. Seyferth and S. P. Hooper, J. Org. Chem., **37**, 4070 (1972).

"Substituted 7-Siladispiro(2.0.2.1)heptanes: the First Stable Silacyclopropanes", R. L. Lambert, Jr., and D. Seyferth, J. Amer. Chem. Soc., **94**, 9246 (1972).

"Halomethyl-Metal Compounds. LIX. An Improved Preparation of Phenyl(fluorodichloromethyl)mercury, A Useful Fluorochlorocarbene Precursor", D. Seyferth and G. J. Murphy, J. Organometal. Chem., **49**, 117 (1973).

"The Insertion of Phenyl(bromodichloromethyl)mercury-derived Dichlorocarbene into the Si-C(ring β C-H Bonds of the *cis* and *trans* Isomers of 1,3-Dimethyl-1-n-butyl-1-silacyclobutane", D. Seyferth, H. Shih, J. Dubac, P. Mazerolles and B. Serres, J. Organometal. Chem., **50**, 39 (1973).

"Halomethyl-Metal Compounds. LXI. Phenyl(fluorodibromomethyl)mercury, A Fluorobromocarbene Precursor", D. Seyferth and S. P. Hopper, J. Organometal. Chem., **51**, 77 (1973).

"Phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury: A Useful Tetrafluoroethylidene Source", D. Seyferth and G. J. Murphy, J. Organometal. Chem., **52**, C1 (1973).

"Halomethyl-Metal Compounds. LXII. Preparation of Diiodomethyl-Metal Compounds", D. Seyferth and R. L. Lambert, Jr., J. Organometal. Chem., **54**, 123 (1973).

"Stereospecific Routes to the Isomeric 7-Bromo-7-lithionorcaranes", D. Seyferth and R. L. Lambert, Jr., J. Organometal. Chem., **55**, C53 (1973).

"Concerning the Reactivity of the Silacyclopropane Ring: Comparison with Ring-Opening Reactions of 1,1-Dimethyl-1-silacyclobutane", D. Seyferth, C. K. Haas and D. C. Annarelli, J. Organometal. Chem., **56**, C7 (1973).

"The Mercuriation of Phosphonate Esters", D. Seyferth and R. S. Marmor, J. Organometal. Chem., **59**, 231 (1973).

"Halomethyl-Metal Compounds. LXIV. The Insertion of Phenyl(bromodichloromethyl)mercury-derived Dichlorocarbene into Benzylic Carbon-Hydrogen Bonds. Stereochemistry and Mechanism", D. Seyferth and Y. M. Cheng, J. Amer. Chem. Soc., **95**, 6763 (1973).

"Halomethyl-Metal Compounds. LXV. Generation of Fluorocarboalkoxycarbenes via the Organomercury Route", D. Seyferth and R. A. Woodruff, J. Org. Chem., **38**, 4031 (1973).

"Synthesis of Heterocyclic Systems via 1,4 Addition Reactions of Phenyl(bromodichloromethyl)mercury-derived Dichlorocarbene", D. Seyferth and H. Shih, J. Amer. Chem. Soc., **95**, 8464 (1973).

"Halomethyl-Metal Compounds. LXVI. The Preparation of C-Tetrachloroaziridines by the Reaction of Carbonimidoxy Dichlorides with Phenyl(bromodichloromethyl)mercury. Fragmentation of Azo- and Azoxyarenes upon Reaction with Phenyl(bromodichloromethyl)mercury", D. Seyferth, W. Tronich and H. Shih, J. Organ. Chem., **39**, 158 (1974).

"Gem-Dichloroallyllithium-A Seemingly Ambident Nucleophile", D. Seyferth, G. J. Murphy and R. A. Woodruff, J. Organometal. Chem., **66**, C29 (1974).

"Dihalocarbene Insertion into the C-H Bonds of Cycloalkanes", D. Seyferth and Y. M. Cheng, Synthesis, 114 (1974).

"Halomethyl-Metal Compounds. LXVII. The Application of Phenyl(trihalomethyl)mercury Compounds in the Synthesis of Highly Halogenated Oxiranes", D. Seyferth, W. Tronich, W. E. Smith and S. P. Hopper, J. Organometal. Chem., **67**, 341 (1974).

"Preparation of Some Functional Halomethyl-Mercury Compounds", D. Seyferth and R. A. Woodruff, J. Organometal. Chem., **71**, 335 (1974).

"The Addition of Gem-Dichloroallyllithium to Aldehydes and Ketones. Unprecedented Ambident Character in the Allylic Metal Reagent Governed by Substrate Electronic Factors", D. Seyferth, G. J. Murphy and R. A. Woodruff, J. Amer. Chem. Soc., **96**, 5011, (1974).

"The Reaction of Phenyl(trihalomethyl)mercury Compounds with Azodicarboxylate Esters. A New Route to Hydrazonodihalomethanes of Type $(RO_2C)_2NN-CX_2$ ", D. Seyferth and H. Shih, J. Organ. Chem., **39**, 2329 (1974).

"The Application of Phenyl(trihalomethyl)mercurials in the Preparation of Heterocyclic Compounds", D. Seyferth and H. Shih, J. Org. Chem., **39**, 2336 (1974).

"A New Route to Highly Substituted 1,3-Disila- and Digermacyclobutanes. The First 1,3-Distannacyclobutane", D. Seyferth and J. L. Lefferts, J. Amer. Chem. Soc., **96**, 6237 (1974).

"The Synthesis of Dimethyl(iodomethyl)tin Iodide and 1,1,3,3,5,5-Hexamethyl-1,3,5-Tristannacyclohexane", D. Seyferth and S. C. Vick, Syn. React. Inorg. Metalorg. Chem., **4**, 515 (1974).

"Halomethyl-Metal Compounds. LXXII. The Preparation of α -Halocyclopropyl Derivatives of Lithium and their Application in the Synthesis of α -Halocyclopropyl Compounds of Silicon, Germanium, Tin, Lead, and Mercury. A Novel Isomerization of syn-7-Bromo-anti-7-lithionorcarane to the anti-7-Bromo-syn-7-lithio Isomer", D. Seyferth, R. L. Lambert, Jr., and M. Massol, J. Organ. Chem., **88**, 255 (1975).

"Halomethyl-Metal Compounds. LXXIII. Grignard Reagents Derived from gem-Dibromocyclopropanes. α -Bromocyclopropyltin Compounds as Precursors for α -Bromocyclopropyllithium Reagents by Transmetalation", D. Seyferth and R. L. Lambert, Jr., J. Organ. Chem., **88**, 287 (1975).

"Halomethyl-Metal Compounds. LXXIV. Organolead Compounds as Precursors for Halocarbenes", D. Seyferth, G. J. Murphy, R. L. Lambert, JR., And R. E. Mammarella, J. Organo. Chem., 90, 173 (1975).

"Halomethyl-Metal Compounds. Part 75. Organomercury Reagents for Room Temperature Dihalocarbene Generation", D. Seyferth and C. K. Haas, J. Org. Chem., 40, 1620 (1975).

"Hexamethylsilirane-A Simple, Isolable Silacyclopropane", D. Seyferth and D. C. Annarelli, J. Amer. Chem. Soc., 97, 2273 (1975)

"Halomethyl-Metal Compounds. LXXVI. α -Bromocyclopropyl Derivatives of Tin and Lead as Cyclopropylidene Precursors", D. Seyferth and R. L. Lambert, Jr., J. Organometal. Chem., 91, 31 (1975).

"Halomethyl-Metal Compounds. LXXVII. An Organomercury Route to Tetrafluoroethyldene", D. Seyferth, G. J. Murphy and R. A. Woodruff, J. Organometal. Chem., 92, 7 (1975).

"The Generation of Dimethylsilylene under Mild Conditions by the Thermolysis of Hexamethylsilirane", D. Seyferth and D. C. Annarelli, J. Amer. Chem. Soc., 97, 7162 (1975).

"Phenyl(trihalomethyl)mercury Compounds: Exceptionally Versatile Dihalocarbene Precursors", D. Seyferth, Acct. Chem. Res., 5, (1972).

"The Elusive Silacyclopropanes-The Preparation and Properties of a Long Sought Class of Organosilicon Compounds", D. Seyferth, J. Organometal. Chem., 100, 237 (1975).

"Organometallic Compounds as Precursors for Fluorinated Carbenes, Chapter in "Carbenes", Vol 2, R. A. Moss and M. Jones, Jr., ed., D. Seyferth, Wiley-Interscience, New York, 1975

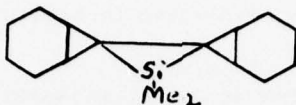
"Highly Halogenated Organic and Organometallic Materials and Strained Ring Organometallics", D. Seyferth, Fin. Tech Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study methods of synthesizing new and useful organometallic compounds and to develop novel methods of synthesis for reaction intermediates. The work included an extensive study of highly halogenated organic and organometallic materials and the synthesis and properties of a number of heretofore unavailable strained ring organometallics. The research results are described in the numerous publications listed above.

More than twenty new organometallic divalent carbon transfer reagents were prepared and evaluated. In the area of new carbene chemistry reactions were studied which involved addition of PhHgCX_3 derived CX_2 to a variety of double bonds. These studies provided some novel, very stable, highly halogenated oxiranes, thiiranes and aziridines, as well as some C, N, O-heterocycles which are difficult to prepare by other routes. Studies of CX_2 insertion into C-H bonds were carried out, including preparatively useful reactions of $\text{PhHgCCl}_2\text{Br}$ with cycloalkanes. It was established that the C-H insertion reaction proceeds with retention of configuration at carbon. A number of halogenated active-metal reagents were prepared as new reagents and their synthetic applicability was examined.

Research with lithium reagents led to the synthesis of the first silacyclopropane.



Silacyclopropanes had been sought, without success by many workers for many years, so the synthesis of this compound was interesting and significant. Related compounds were prepared by similar reactions. The compounds were found to be quite stable thermally, but highly reactive. (They react exothermally, at room temperature with oxygen, water, alcohols, ammonia, carbon tetrachloride, sulfur, etc., -- behavior typical of known cyclic tetraorganosilicon compounds.) In related work, the smallest stannacarboxylic compound known to date was prepared.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Photochemical Addition of Benzene to Unsaturated Materials
2. PRINCIPAL INVESTIGATOR: Dr. R. Srinivasan
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598
3. INCLUSIVE DATES: 1 December 1971 - 30 November 1975
4. CONTRACT NUMBER: F44620-72-C-0024
5. COSTS AND FY SOURCE: \$35,155 FY72
37,074 FY73
22,240 FY74
29,989 FY75
16,788 FY76
6. SENIOR RESEARCH PERSONNEL: Dr. J. Cornelisse
Dr. G. Subrahmanyam
Dr. J. A. Ors
Dr. C. S. Angadiyavar
7. JUNIOR RESEARCH PERSONNEL: V. Y. Merritt
L. Garwin
R. Kaiser
A. Burkett
8. PUBLICATIONS:

"Stereochemistry of the (2'-Vinylcyclopropyl) Cyclobutane Rearrangement. Photochemical 1,3-Addition of Benzene to 3,4-Substituted Cyclobutenes", R. Srinivasan, J. Amer. Chem. Soc., **94**, 8117 (1972).

"Thermal Decomposition of Cis, trans, cis-1,2-dideuterio-3,4-Dimethylcyclobutane", R. Srinivasan and J. N. C. Hsu, Chem. Comm., 1213 (1972).

"Thermal Rearrangement of Pentacyclo [6.5.0.0²,4.0³,7.0¹⁰,13] trideca-5,11-diene", R. Srinivasan, Tetrahedron Ltrs., 4537 (1972).

"The Reactive State in the Photochemical Addition of Benzene and Alkylbenzenes to Cycloalkenes", J. Cornelisse and R. Srinivasan, Chem. Phys. Ltrs., **20**, 278 (1973).

"Reaction of Diiron Nonacarbonyl with Bridged Polycyclics Containing the Vinylcyclopropane Group", R. M. Moriarty, C-L Yeh and R. Srinivasan, Tetrahedron Ltrs., 5325 (1972).

"Photochemical 1,3-Addition of Benzene to Olefins. Orientational Specificity Induced by Methyl Substituents on Aromatic and Olefinic Rings", J. Cornelisse, V. Y. Merritt and R. Srinivasan, J. Am. Chem. Soc., **95**, 6197 (1973).

"Thermal Decomposition of Tetracyclo (5.3.0.0²,10.0³,6) deca-4,8-diene. An Unusual Disproportionation Reaction", R. Srinivasan, Tetrahedron Ltrs., 4029 (1973).

"Synthesis of [4.3.3] Propellanes by the Photochemical Addition of Tetralen to Olefins", C. S. Angadiyavar, J. Cornelisse, V. Y. Merritt and R. Srinivasan, ibid. 4407 (1973).

"Photochemical Addition of Benzene to Cyclopentene" V. Y. Merritt, J. Cornelisse and R. Srinivasan, J. Am. Chem. Soc. **95**, 8250 (1973).

"Photochemical 1,3-Addition of Anisole to Cyclopentene. A Stereospecific Synthetic Route to Perhydroazulenes", R. Srinivasan, V. Y. Merritt, and G. Subrahmanyam, Tetrahedron Ltrs., 2715 (1974).

"Thermal Rearrangements of the Photochemical 1,3-Adducts of Benzene to Methylenecyclobutane", R. Srinivasan, ibid., 2725 (1974).

"Chemical Transformations of the Photochemical 1,3-Adducts of Benzene and Anisole to Cyclobutenes", G. Subrahmanyam and R. Srinivasan, Tetrahedron, 31, 1797 (1975).

"Acid Catalysed Cleavage of the 1,3-Photoadduct of Benzene and cis-3,4-dichlorocyclobutene: Structure of the p-Nitrobenzoate of 2,5-endo-3,4-cis-dichloro-anti-10-hydroxytricyclo [4.3.1.0^{2,5}] dec-8-ene", G. Subrahmanyam, R. Srinivasan, S. J. LaPlaca, and J. E. Weidenborner, J. C. S. Chem. Comm. 231, (1975).

"Photochemical 1,3-Addition of Anisole to Olefins: Mechanistic Studies", J. A. Ors and R. Srinivasan (in preparation).

"Photochemical 1,3-Adducts of Anisole to Olefins: Structure Studies", J. A. Ors and R. Srinivasan (in preparation).

"Photochemical Addition of Benzene to Unsaturated Materials" R. Srinivasan, Fin. Tech Rpt.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aims of this work were (1) a systematic study of the mechanistic and kinetic aspects of the photochemical 1,3-addition of benzene and its derivatives to olefins; (2) the utilization of the 1,3-photoaddition reaction as a route to the synthesis of cage compounds and natural products.

The photoaddition reactions of benzene, several alkylbenzenes, and anisole to a variety of olefins were systematically investigated. The identities of the numerous products that were obtained were established. Kinetic data over a range of concentrations of the olefin were measured. From an analysis of these results, it was possible to exclude the diradical ("prefulvene") mechanism that had been proposed for these reactions by a group in England, and instead, suggest an alternative mechanism which was based on the formation of an exciplex between the singlet excited state of the aromatic compound and the olefin. From a detailed model for this exciplex, it has become possible to predict the preferred stereochemistry and photochemical efficiency of the addition between different olefins and a given aromatic reactant.

The intermediacy of exciplexes in many photochemical reactions has come to the attention of the photochemists in recent years. The systems that were investigated under this contract offer highly favorable features for further investigations of the general phenomenon of exciplex photochemistry.

The exploitation of the photochemical 1,3-addition as a useful synthetic route was made possible by the discovery that anisole participated in this reaction as readily as benzene, but the product was - unlike the benzene photoadduct - stable towards photodegradation. As a result, photoadducts of anisole could be prepared in yields as high as 80 percent whereas benzene typically gave only a 30 percent yield. It was also established that the anisole photoadduct could be decomposed by acid, even without being isolated, to give rise to useful polycyclic bridged ketones. In turn these have been converted to perhydroazulenes which are synthons for a class of naturally occurring terpenes.

The photochemical 1,3-adduct of benzene to cyclobutene underwent a novel thermal rearrangement, viz. the (2'-vinycyclopropyl) cyclobutane rearrangement, which was described for the first time in this work. The synthetic scope and stereochemistry of this reaction were studied in detail. It was established that this reaction offers one of the easiest routes to the synthesis of the triquinacene skeleton.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Second Summer Colloquium on Electronic Transition Lasers

2. PRINCIPAL INVESTIGATOR: Dr. J.I. Steinfeld
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

3. INCLUSIVE DATES: 1 June 1975 - 31 May 1976

4. GRANT NUMBER: AFOSR-75-2826

5. COSTS AND FY SOURCE: \$5,182 FY75

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Electronic Transition Lasers/Proceedings of Second Summer Colloquium", edited by J. I. Steinfeld, published by M.I.T. Press (Jul 1976)

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Increased Air Force capabilities in reconnaissance, communication, and weaponry require developments in laser technology and new lasers operating at shorter wavelengths. Since there is presently a lack of suitable short wavelength lasers that are required for certain AF mission areas, it was felt desirable to conduct a workshop on electronic transition lasers. At this workshop, researchers in the field presented the results of their research, conducted an open interchange of ideas, and evaluated and assessed progress in this area.

The colloquium/workshop was held at the facilities of the Marine Biological Laboratories in Woods Hole, Mass., in September 1975. There were one hundred forty registered participants, the number being limited by the size of the facilities. Approximately fifty papers were presented in five technical sessions.

The workshop was extensively reported by Laser Focus magazine in its December 1975 issue, and was characterized as one of the "eleven principal international meetings of 1975." Complete proceedings were published by the M.I.T. Press in July 1976.

AFOSR Program Manager: Lt Col J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: The Chemical Kinetics of Some Elementary Reactions of Oxygen Atoms.

2. PRINCIPAL INVESTIGATOR: Dr. Richard B. Timmons
Department of Chemistry
Catholic University
Washington, D.C.

3. INCLUSIVE DATES: 1 June 1972 - 29 February 1976

4. GRANT NUMBER: AFOSR-72-2378

5. COSTS AND FY SOURCE: \$25,619 FY72; \$25,000 FY 73; \$25,000 FY75.

6. SENIOR RESEARCH PERSONNEL: None.

7. JUNIOR RESEARCH PERSONNEL: J. H. Lee
C. N. Wei
V. T. Rivas
R. J. Bonanno

8. PUBLICATIONS:

"ESR Study of the Kinetics of the Reactions of $O(^3P)$ Atoms with CS_2 and OCS ",
C. N. Wei and R. B. Timmons, J. Chem. Phys., **62**, 3240 (1975).

"The Kinetics and Mechanism of the Reaction of $O(^3P)$ Atoms with CH_3CN and CF_3CN ",
R. J. Bonanno, R. B. Timmons, L. J. Steif and R. B. Klemm, submitted to J. Chem. Phys.

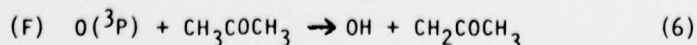
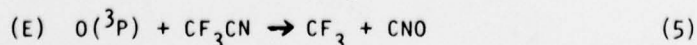
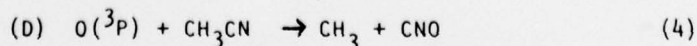
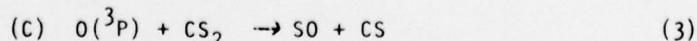
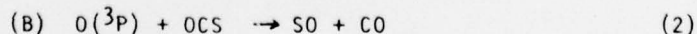
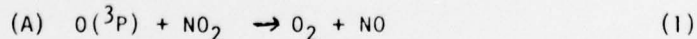
"Atmospheric Oxidation of Nitriles", R. B. Timmons and R. B. Klemm, to be submitted to Science.

"Kinetics and Mechanism of the Reactions of $O(^3P)$ with Acetone", J. H. Lee and R. B. Timmons, in preparation.

"The Chemical Kinetics of Some Elementary Reactions of Oxygen Atoms", R. B. Timmons, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research studies involved the investigation of the kinetics and mechanism of selected gas phase reactions of ground state oxygen atoms. All of the reactions studied are of either direct or indirect interest with respect to oxidative processes which occur in the atmosphere. Among the reactions studied were the following:



Each reaction was studied over wide temperature ranges using fast flow apparatus coupled with electron spin resonance and/or mass spectrometric detection methods. In some cases, (with CH_3CN and CF_3CN) it was necessary to use the flash photolysis-resonance fluorescence method in order to avoid the problem of free radical chain reactions observed under typical flow tube conditions. The specific rate constants obtained are expressed in terms of the usual Arrhenius equation.

AFOSR Program Manager: A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Gas Phase Spectrometry Methods - Trace Analysis of Elements and Analytical Gas Phase Spectrometry and Combustion Diagnostics
2. PRINCIPAL INVESTIGATOR: Dr. James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, FL 32611
3. INCLUSIVE DATES: 1 September 1973 - 31 August 1975
4. GRANT NUMBER: AFOSR-74-2574
5. COSTS AND FY SOURCE: \$71,062 FY73; \$75,000 FY74
6. SENIOR RESEARCH PERSONNEL:

Dr. N. Zorov	Dr. D. Johnson
Mr. F. VanGeel	Dr. R. Avni
Dr. D. Stojanovic	Dr. R. Dininny
Dr. J. McHard	Dr. P. E. Walters
Dr. R. Michel	
7. JUNIOR RESEARCH PERSONNEL:

D. O. Knapp	J. J. Fitzgerald
C. J. Molnar	W. K. Fowler
F. S. Chuang	L. P. Hart
M. Blackburn	J. Messman
G. Boutilier	B. Pollard
J. Bradshaw	B. W. Smith
C. Chen	S. Weeks
T. L. Chester	
8. PUBLICATIONS:

"Optimization of Thermostated Electrodeless Discharge Lamps for Analytical Atomic Spectrometry", R. F. Browner and J. D. Winefordner, Spectrochim. Acta 28B, 263 (1973).

"Pulsed Source Atomic Fluorescence Spectrometry", N. Omenetto, M. Fraser, and J. D. Winefordner, Appl. Spectrosc. Rev. 7, 147 (1973).

"Non-Linear Optical Behavior in Atomic Fluorescence Flame Spectrometry", N. Omenetto, P. Bennetti, L. P. Hart, J. D. Winefordner, and C. Th. J. Alkemade, Spectrochim. Acta 28B, 289 (1973).

"On the Shape of Atomic Fluorescence Analytical Curves with a Laser Excitation Source" N. Omenetto, L. P. Hart, P. Bennetti, and J. D. Winefordner, Spectrochim. Acta 28B, 301 (1973).

"Information Theory and its Use to Analytical Chemistry", J. J. Fitzgerald and J. D. Winefordner, Rev. Anal. Chem., in press.

"Simultaneous Multielement Atomic Emission Flame Spectrometry with an Image Vidicon Detector", D. O. Knapp, N. Omenetto, F. Plankey, L. Hart, and J. D. Winefordner, Anal. Chim. Acta 69, 455 (1974).

"Double Modulation Atomic Fluorescence Flame Spectrometry", W. K. Fowler, D. O. Knapp, and J. D. Winefordner, Anal. Chem. 46, 601 (1974).

"Jet Engine Oil Analysis by Atomic Absorption Spectrometry with Graphite Element", F. S. Chuang and J. D. Winefordner, Appl. Spectrosc. 28, 215 (1974).

- "On the Use of a Power Divider for Thermostated Electrodeless Discharge Lamps in Atomic Fluorescence Spectrometry", D. O. Knapp, C. J. Molnar, and J. D. Winefordner, Anal. Chem. 46, 622 (1974).
- "Review of Multielement Atomic Spectroscopic Methods", J. D. Winefordner, J. J. Fitzgerald, and N. Omenetto, Appl. Spectrosc., in press.
- "Hadamard Spectrometer for UV-Visible Spectroscopy", F. W. Plankey, T. H. Glenn, L. P. Hart, and J. D. Winefordner, Anal. Chem. 46, 1000 (1974).
- "Flame Spectrometry", J. D. Winefordner, and T. J. Vickers, Anal. Chem. 46, 192R (1974).
- "Vitreous Carbon Furnace With Continuous Sample Introduction for Atomic Fluorescence Spectrometry", C. J. Molnar and J. D. Winefordner, Anal. Chem. 46, 1419 (1974).
- "Effects in Ultraviolet and Visible Spectrophotometric Measurements Caused by Multiple Reflections Within the Cell", C. T. Chen and J. D. Winefordner, Can. J. Spectrosc. 19, 120 (1974).
- "A New Discrete Atomization Cell for Atomic Fluorescence Spectrometry", C. J. Molnar and J. D. Winefordner, Anal. Chem. 46, 1807 (1974).
- "Comparison of CW and Pulsed Continuum Sources for Atomic Fluorescence Flame Spectrometry" D. J. Johnson, F. W. Plankey, and J. D. Winefordner, Anal. Chem. 46, 1898 (1974).
- "Atomic Fluorescence Spectrometry: Past, Present and Future", J. D. Winefordner, Chem. Tech., February 1975.
- "Emission from Atomic Vapor Produced in Tubular Vitreous Carbon Furnace", C. J. Molnar, F. S. Chuang, and J. D. Winefordner, Spectrochim. Acta 30B, 183 (1975).
- "Analysis of Wear Metals in Jet Engine Oils Via Atomic Fluorescence Flame Spectrometry with a Continuum Source", D. J. Johnson, F. W. Plankey, and J. D. Winefordner, Can. J. Spectrosc. 19, 151 (1974).
- "Interference of Magnesium by Trace Concomitants in Flame Atomic Absorption Spectrometry", C. Chen and J. D. Winefordner, Can. J. Spectrosc. published.
- "Some Considerations on the Microwave Electrodeless Discharge Plasma Diagnostics in Argon, Helium or Nitrogen Atmospheres", R. Avni and J. D. Winefordner, Spectrochim. Acta B, in press.
- "Single Channel Methods (Sequential and Multiplex) vs Multichannel Methods in Optical Spectroscopy" J. D. Winefordner, R. Avni, T. L. Chester, L. P. Hart, J. J. Fitzgerald, D. J. Johnson, and F. W. Plankey, Spectrochim. Acta B, in press.
- "On the Use of Wien and Planck Radiance Expressions for Emission and Fluorescence in Flames", N. Omenetto and J. D. Winefordner, Spectrochim. Acta B (note), in press.
- "Evaluation of the Analytical Capabilities of Frequency Modulated Sources in Multi-Element Non-Dispersive Flame Atomic Fluorescence Spectrometry", T. L. Chester, and J. D. Winefordner, Spectrochim. Acta B, (note) in press.
- "Atomic Fluorescence Spectrometry with an EIMAC Continuum Excitation Source and A Graphite Filament Atomizer", F. S. Chuang, and J. D. Winefordner, Appl. Spectrosc., published.

"Multi-Element Analysis Via Rapid-Scan Computer Controlled Atomic Fluorescence Spectrometry, Using a Continuum Source", D. J. Johnson, F. W. Plankey, and J. D. Winefordner, Anal. Chem., published.

"Evaluation of an EIMAC Lamp as an Excitation Source for Condensed Phase Molecular Fluorescence. Application to the Quantitation of the Ergot Alkaloids in Biological Fluids by High-Pressure Liquid Chromatography", R. J. Perchalski, J. D. Winefordner and B. J. Wilder, Anal. Chem., in press.

"Selectively-Modulated Interferometric Dispersive Spectrometer for UV-Visible Atomic and Molecular Spectrometry", J. J. Fitzgerald, T. L. Chester, and J. D. Winefordner Anal. Chem., in press.

"A New Hydrolysis Procedure For Preparation of Orange Juice for Trace Element Analysis by Atomic Absorption Spectrometry", J. A. McHard, J. D. Winefordner, and J. A. Attaway, J. Ag. Food Chem., in press.

"Theoretical Comparison of Fourier Transform Spectrometry with Single Slit Linear and Slew Scan Spectrometric Methods for the Photon Noise Limited Situation", T. L. Chester, J. J. Fitzgerald, and J. D. Winefordner, Appl. Opt. submitted.

"Some Applications of the Use of a Pulsed N₂ Laser in Analytical Spectroscopy of Molecules in the Condensed Phase", T. F. VanGeel and J. D. Winefordner, Anal. Chem. submitted.

"Analytical Applications of Laser Excited Fluorimetry of Molecules in the Condensed Phase", B. W. Smith, F. W. Plankey, N. Omenetto, L. P. Hart, and J. D. Winefordner, Spectrochim. Acta 30A, 1459 (1974).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The AFOSR program on Gas Phase Spectrometry, Trace Analysis of Elements, and Combustion Diagnostics at the University of Florida consists of fundamental, instrumental, methodological and applied studies of atomic and molecular emission and luminescence and atomic and molecular absorption spectrometric methods, particularly as these measurement methods apply to trace element analysis, diagnostics of plasmas, and optimization of spectrometric experimental methods of analysis. By means of such studies, new and improved selection, sensitive, precise, accurate, and rapid methods of trace analysis of elements and molecules in the gas phase or convertible to the gas phase have been or are being developed and as an additional bonus valuable diagnostic methods and results for plasmas result. Special efforts have been given to rapid simultaneous or sequential multi-element methods of analysis of elements, particularly as applied to the trace analysis of many elements.

Fundamental Studies: A variety of physical and spectroscopic parameters either characteristic of the plasma, e.g., atmospheric pressure flames, low pressure Rf inductively coupled plasma, or microwave capacitatively coupled plasma, such as the plasma temperatures (gas temperature, excitation temperature, i.e., electronic, vibrational, and rotational, electron temperature, and ion temperature) and ion densities have been measured by both spectroscopic and electric probe techniques. The spectroscopic and electric probe methods are well described in the literature, e.g., R. H. Huddleston and S. L. Leonard, "Plasma Diagnostic Techniques", Academic Press, New York, 1965. These measurements have shown that the ion densities in microwave plasmas of inert gases, as Ar and Ne, and in inert gases containing metals, e.g., Tl, Ti, etc., are lower than in equivalent Rf plasmas, whereas the electron temperatures are in the reverse order. Such measurements are useful in the design of sealed-off EDLs (electrodeless discharge lamps) as excitation sources in atomic absorption and atomic fluorescence spectrometry.

A thorough experimental optimization of sealed-off EDLs for several elements (Zn, Tl, Mn, Pb, and Hg) has also been performed. This latter study demonstrated the importance of thermostating the EDLs during operation. More recently, a concentrated experimental optimization program has been initiated on EDLs for atomic fluorescence spectrometry and are utilizing the SIMPLEX statistical approach. Certain steps in the preparation and operation of EDLs (via A-antennas) have been shown to be critical, including thermostating as mentioned above and the outgassing step (time and method).

The influence of source intensity upon the atomic fluorescence signals and the shape of analytical calibration curve (fluorescence intensity vs analyte concentration) has also been looked at in detail. It has been theoretically shown and experimentally verified that: (1) the atomic fluorescence signal increases linearly with source intensity until saturation is approached where the fluorescence signal reaches a constant plateau; (2) if saturation is approached, the fluorescence signal is nearly independent to source fluctuations and quantum efficiency; (3) if saturation is nearly reached, source scatter is even more difficult to deal with; (4) if saturation is nearly reached, analytical calibration curves have extended linearity at high analytical concentrations. Saturation is nearly achieved only if laser sources are used. A N_2 -pumped dye laser has been used for elements with strong absorption lines at wavelengths greater than about 360 nm.

Molecular fluorescence as well as Raman spectrometry also benefits from the use of lasers. Extremely low detection limits results for molecules which can be excited with either the N_2 -laser alone or with the N_2 -laser/dye laser combination. It is doubtful, however, whether saturation is even approached and so the molecular fluorescence intensity varies linearly with laser power. Raman scatter is useful for quantitative analysis of molecules in solution if present at concentrations $\geq 0.1\%$.

Radiance expressions for atomic emission and atomic fluorescence including the effect of stimulated emission have been derived to consider the exact effect of self-absorption on the fluorescence and thermal emission processes. For the case of thermal emission, if stimulated emission can be accounted for, then

$$B_E = A_t^* \frac{P_l}{B_{v_o}} (T_f)$$

where A_t^* is the total absorption factor in which stimulated emission is accounted for and $B_{v_o}^{Pl}(T_f)$ is the Planck spectral radiance at the line center, v_o , and at the temperature of the hot gases, T_f . If stimulated emission is negligible, then $B_{v_o}^{Pl}(T_f)$ can be replaced by the Wien approximation, $B_{v_o}^{Wi}(T_f)$.

Several papers have been written and are in press concerning a systematic comparison of the signal-to-noise ratios for multielement spectroscopic measurement methods, including methods based upon sequential linear scan, sequential slewed scan, multichannel, and multiplex techniques. It is shown that for the UV-Visible-Near IR region that the multiplexed methods (based on Fourier Transform or Hadamard Transform) have little if any use for real analytical systems. It is also shown

that the multichannel methods is always the best but is often too expensive, bulky, and complex as compared to the other non-multiplexed methods, and therefore, in terms of speed, cost, and analytical figures of merit, the sequential slewed method is recommended.

Methodological and Instrumental Studies. Pulsed light sources have been used in both atomic and molecular spectrometric studies. Pulsed non-laser sources are shown to have benefit over cw non-laser sources if the noise of the system is predominately due to the detector. Pulsed laser sources have benefit in atomic fluorescence signals. Detection limits of elements in flames excited via a N_2 -pumped dye laser are essentially as good as or better than any of the previous atomic fluorescence flame spectrometric results obtained with cw non-laser sources. The prediction that laser sources show result in detection limits 4-6 orders of magnitude lower than non-laser sources, especially for non-resonance fluorescence lines, has not yet born out. Studies are in progress to determine the noise sources in both systems. Finally, a pulsed N_2 -laser with or without a dye laser (either narrow band or broad band) is an excellent source for molecular fluorescence and Raman Spectrometry; the system consists of the laser source, a quartz cell with the sample, a monochromator, a photomultiplier, and a boxcar integrator synchronized to the laser pulse. Time resolution aids in resolving two or more species with similar molecular fluorescence spectra. Gas phase molecular fluorescence spectra has also been measured; in this case, separation of molecular species is via a gas chromatograph and the molecules are excited as they pass through a 3-mm square quartz cell.

A general, versatile, intense, non-laser cw source for atomic fluorescence is the EIMAC xenon arc lamp; this is a point source at the focus of a parabolic reflector and has a sapphire window. It is an excellent source for atomic fluorescence, molecular fluorescence, and photochemical studies. It has been used in atomic fluorescence spectrometry and detection limits approaching those obtained with optimized EDLs result. It has also been used as the source of excitation for a fluorimetric detector in gas chromatography and in liquid chromatography.

During the past two years, many different multielement methods have been studied. The Hadamard Transform atomic fluorescence/emission flame spectrometer proved to be flame background noise limited. The SIT vidicon tube detector atomic fluorescence/emission spectrometer proved to be detector noise limited, wavelength range limited, and signal limited. The computer-controlled slewed scan dispersive spectrometer atomic fluorescence system has proven to be an excellent system for determination of trace elements in real samples, e.g., jet engine oil samples, blood sera, geological samples, etc. More recently, a computer-controlled slewed scan selectively modulated interferometric dispersive spectrometer (SEMIDS) has been developed and has been shown to be not only novel and exciting but most likely the spectral method for rapid, multielement analysis. In SEMIDS, a Michelson interferometer is constructed except that the stationary mirror is replaced with a computer controlled stepping rotating grating; at any given grating angle, a certain small wavelength range will undergo constructive interference with the modulated white light component from the other arm of the Michelson interferometer resulting in a modulated spectral component at the grating setting. The real advantage of SEMIDS is the simultaneous high resolution and large throughput, e.g., a 5-mm entrance aperture results in a large signal but only ~35% drop in the theoretical resolution of the grating.

In addition to light source development, non-flame furnace atomizers have also been studied. A graphite filament atomizer with or without a flame sheath has been shown to be valid for some trace elements in several real samples. In addition, a continuous flow tube furnace with sample being continuously aspirated into the furnace has also been shown to be useful for ultra-trace analysis of volatile elements, e.g., Cd, Zn, Pb, As, Fe, Mn, Mg, etc. All non-flame cells have some difficulties with refractory elements and matrices, e.g., Cd in alumina and even Cd in sea water. Interference studies with these devices as well as development of an atomization theory are in progress.

Other studies performed have included the use of a power divider to operate 2 EDLs from the same microwave power supply, double modulation (chopped EIMAC source and wavelength modulation) atomic fluorescence spectrometry, estimation of the reflection losses in absorption cells, and the use of an EIMAC continuum cw source for atomic fluorescence spectrometry of trace elements atomized with a graphite filament.

Applied Studies. They have continued studies involving measurement of trace elements in jet engine oils, biological samples, foods, and environmental samples. For example, a recent study has shown that there is considerable lead in some food wrappers. An excellent hydrolysis procedure has been developed for orange juice; the hydrolysate is then determined by atomic absorption furnace or flame spectrometry or by atomic emission plasma jet spectrometry.

The molecular fluorescence and phosphorescence characteristics of Rhodamine complexes with gallium and indium have also been studied.

Reviews. During the past two years, another biannual review on flame spectrometry has been written and published. Other reviews include one on pulsed light sources in atomic fluorescence spectrometry, one on multielement methods of analysis and one on atomic fluorescence spectrometry.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Electrode Mechanisms Using Reflection and Electron Spectroscopy
2. PRINCIPAL INVESTIGATOR: Professor Nicholas Winograd
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3. INCLUSIVE DATES: 15 January 1972 - 14 January 1976
4. GRANT NUMBER: AFOSR-72-2238
5. COSTS AND FY SOURCE: \$43,378 FY72; \$30,755 FY74; \$30,847 FY75
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8. PUBLICATIONS:

"Application of Coulostatic Charge Injection Techniques to Improve Potentiostat Risetimes", J. E. Davis and N. Winograd, Anal. Chem., **44**, 2152 (1972).

"An Implicit Finite Difference Method. Simulation of Spectroelectrochemical Working Curves", N. Winograd, J. Electroanal. Chem. and Interfac. Electrochem., **43**, 1-8 (1973).

"Observation of Polymorphic Lead Monoxide Surfaces Using X-Ray Photoelectron Spectroscopy", K. S. Kim and N. Winograd, Chem. Phys. Lett., **19**, 209 (1973).

"X-Ray Photoelectron Spectra of Lead Oxides" K. S. Kim, T. J. O'Leary and N. Winograd, Anal. Chem. **45**, 2214 (1973).

"X-Ray Photoelectron Spectroscopic Studies of Palladium Oxides and the Palladium-Oxygen Electrode", K. S. Kim, A. F. Gossman and N. Winograd, Anal. Chem., **46**, 197 (1974).

"ESCA Studies of Metal and Metal Electrode Surfaces", K. S. Kim, C. D. Sell and N. Winograd, in "Processings of the Symposoin on Electrocatalysis," The Electrochemical Society, edited by Manfred W. Breiter, 1974, p. 242.

"Nichrome Resistor Failures as Studied by X-Ray Photoelectron Spectroscopy (XPS or ESCA)", W. E. Baitinger, N. Winograd, J. W. Amy and J. Munarin, in "12th Annual Proceedings of the Reliability Physics 1974", IEEE Devices and Reliability Groupd, 1974, p. 1.

"ESCA Studies of Metal-Oxygen Surfaces Using Argon and Oxygen Ion-Bombardment", K. S. Kim, W. E. Baitinger, J. W. Amy and N. Winograd, J. Electron. Spectrosc. **5**, 351 (1974).

"XPS Studies of Interactions in Multicomponent Metal and Metal Oxide Thin Films" N. Winograd, W. E. Baitinger, J. W. Amy and J. Munarin, Science, **184**, 565 (1974).

"X-Ray Photoelectron Spectroscopic Studies of Nickel-Oxygen Surfaces Using Oxygen and Argon Ion-Bombardment", K. S. Kim and N. Winograd, Surface Sci., **43**, 625 (1974).

"X-Ray Photoelectron Spectroscopic Studies of Ruthenium-Oxygen Surfaces", K. S. Kim and N. Winograd, J. Catalysis, **35**, 66 (1974).

"Charge Transfer Transition Accompanying X-Ray Photoionization in Transition-Metal Compounds", K. S. Kim, J. Electron Spectrosc., **3**, 217 (1974).

"X-Ray and UV Photoemission Studies of Valence Electronic Structure of NiO", K. S. Kim, Chem. Phys. Lett. **26**, 234 (1974).

"X-Ray Photoelectron Spectroscopic Binding Energy Shifts Due to Matrix in Alloys and Small Supported Metal Particles", K. S. Kim and N. Winograd, Chem. Phys. Lett., **30**, 91 (1975).

"Charge Transfer Shake-up Satellites in X-Ray Photoelectron Spectra of Cations and Anions of SrTiO_3 , TiO_2 and Sc_2O_3 ", K. S. Kim and N. Winograd, Chem. Phys. Lett., **31**, 312 (1975).

"X-Ray-Photoelectron Spectroscopic Studies of the Electronic Structure of CoO ", K. S. Kim, Phys. Rev. B, **11**, 2177 (1975).

"X-Ray Photoelectron Spectroscopic Studies of Cadmium-Silver-Oxygen Surfaces", J. S. Hammond, S. W. Gaarenstroom and N. Winograd, Anal. Chem. **47**, 2193 (1975).

"X-Ray Photoelectron Spectroscopic Studies of PbO Surfaces Bombarded with He^+ , Ar^+ , Xe^+ , and Kr^+ ", K. S. Kim, W. E. Baitinger and N. Winograd, Surface Sci., **55**, 285 (1976).

" $L_{2,3}M_{23}M_{23}$ Auger Energies of Metallic Ni, Cu and Zn; Evidence for 3d-4s Admixed Screening in Ni", K. S. Kim, S. W. Gaarenstroom and N. Winograd, Phys. Rev. B., in press.

"Calculation of $L_{2,3}M_{45}M_{45}$ Auger Energies of Metallic Ni, Cu and Zn", K. S. Kim, S. W. Gaarenstroom, and N. Winograd, Chem. Phys. Lett., in press.

9. ABSTRACT OF ACCOMPLISHMENTS AND OBJECTIVES:

The major effort of the research has been to develop both IRS and XPS (X-ray photoelectron spectroscopy) as viable spectroscopic tools in characterizing electrode surfaces. To date, these studies have involved characterizing electrode surfaces. To date, these studies have involved the development of the internal reflection spectroscopic (IRS) technique at optical transparent electrodes (OTE's) to monitor in situ surface electrode reactions. Reflection changes induced both by the diffusion of light absorbing species in solution, and by the alteration of the optical constants associated with the formation of electrode films have been observed. In addition, in 1971 the first experiments were initiated utilizing electron spectroscopy for chemical analysis (XPS or ESCA) for identifying the nature of surface films. Since that time the concern has been with developing XPS as a mechanistic aid in following electrode reactions, primarily those where surface oxide films alter the electronic properties of the electrode surface. These studies on well defined oxides have been invaluable in providing the data base for the results obtained on oxides generated in electrochemical cells. These studies on oxide

systems have now been extended to characterizing a variety of metal ions deposited at underpotential with a special interest in understanding the XPS chemical shift of these species versus the corresponding bulk species.

Initial studies focused on the lead oxygen system. The Pb4f and O 1s binding energies for the bulk compounds PbO (rhombic), PbO (tetragonal), Pb₃O₄ and PbO₂ were obtained. By preparing a clean lead surface in situ, the various stages of surface oxidation were monitored by exposing the sample to varying amounts of oxygen and comparing the results to the spectra of the known oxides. For oxide films of thickness on the order of one monolayer, three different oxygen species were observed including chemisorbed oxygen atoms, rhombic PbO and tetragonal PbO. As the oxidation increased to several monolayers, the rhombic structure predominated in accord with results predicted by X-ray diffraction studies.

XPS was found to be extremely powerful in elucidating the nature of hydrates of metal oxides. By exposure of PbO₂ to water vapor, two different oxygen species were seen in the O 1s spectrum. Since mass spectrometric analysis indicated 0% bulk water, the observed water must only be present on the surface. Similar studies on the hydrates of RuO₂ indicates the presence of bulk water.

Another system of extremely important catalytic interest is the Ni-oxygen system. The surface chemistry of Ni was studied using both temperature changes and ion bombardment as techniques for elucidating electrode structure. The major finding of this work is that the XPS technique could distinguish the presence of a surface cation defect structure, Ni₂O₃, present in varying degrees, on oxidized Ni surfaces.

Since 1971, numerous, complex approaches have been espoused to ingeniously remove the solution layer from an electrode surface so it can be inserted into a high vacuum spectrometer.

A rather simple procedure has been developed that has been quite effective in performing initial survey work for many systems. The approach employs a small volume electrochemical cell (~150 μ l) placed within a high quality controlled atmosphere box (O₂, H₂O < 5 ppm) which also encloses the sample introduction rod to the XPS spectrometer. The cell can be aspirated under potentiostatic control within several milliseconds and can be inserted into the 10⁻⁹ torr vacuum of the XPS analyzer within 60 seconds. Maximum contamination of 1/3 of a monolayer of oxygen or carbon is observed on Pt electrodes exposed to water. The electrode can be withdrawn from the spectrometer, and the solution replaced on the electrode while it is under potentiostatic control, for reexamination of electrochemical properties. Although these contamination levels are not as low as those proposed by using the in situ thin layer cells, many important initial studies can be performed quickly.

This cell configuration has been exploited to study the Pt electrode surface, using both in situ IRS studies, and conventional electrochemical techniques to verify the integrity of the electrode surface.

Comparison of XPS studies to coulometric investigations has clearly been valuable in lending credence to the XPS approach. Comparing XPS and reflection spectroscopic studies on Pt oxidized in situ for further verification of the proposed results, was the goal. Of special interest has been the development of the internal reflection (IRS) mode, since with the possible exception of scanning ellipsometry, it offers the only approach to complete characterization of all the optical constants (n, k, and H) of the platinum oxide layer.

efforts in this direction resulted in the design of a computer controlled IRS spectrometer, the implementation of a sophisticated curve fitting routine for inversion of the Fresnel formulae, and the capability of measuring optical constants, for both the optically transparent platinum electrode and the oxide overlayer. The procedure for extracting these results involved massive data collection as the angle of incidence, polarization, wavelength and electrode potential are varied. The curve-fitting routine then appropriately weights each datum using Hansen's equations for a multilayer film system. The optical constants of the bare OTE are first determined and then input to the data processing of the reflectivities measured during electrochemical production of the absorbed film. The measured thickness of the Pt film is independent of wavelength to a standard deviation of 1.5%, illustrating the unprecedented power of this approach in analyzing thin absorbing films, and demonstrating the utility of the IRS spectrometer.

The same procedure can be followed measuring the optical properties of thin films absorbed on the OTE using a 4-layer optical model. Results to date show a linear thickness vs. potential plot for platinum oxide formation between 0.6V and 1.8V vs SCE in H_2SO_4 , where the growth reaches limiting value of 8\AA . These thicknesses are in excellent agreement with the ellipsometrically measured thickness recently reported for the formation of oxide on Pt.

These measurements are consistent with the thickness measurements evaluated by XPS, at least at 1.8V. The agreement of the two approaches yields strong evidence that the vacuum transfer techniques are valid ones for these films. Similar XPS studies on oxides generated below 1.0V vs. SCE, however, do not yet produce thickness consistent with the IRS techniques that the very thin films may be soluble or may pump off in the vacuum. Future studies using XPS, Auger or LEED must clearly take these problems into account. Thus, if film integrity can be confirmed by IRS, XPS becomes the most powerful probe for identification of its chemical composition. In this case, the conclusive identification of PtO by XPS illustrates this point.

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